

## Supporting Information

### Hole Transfer Processes in *meta*- and *para*-Conjugated Mixed Valence Compounds: Unforeseen effects of bridge substituents and solvent dynamics

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#### Alternative electron transfer theories

Case I) In the strong diabatic limit (electronic coupling  $V \ll k_B T$ ) equation (S1) holds as derived by perturbation theory (Fermi's Golden Rule) with prefactor  $A_{PT}$  depending on the square of the electronic coupling  $V$ :

$$A_{PT} = \frac{2\pi}{\hbar} \frac{V_{12}^2}{\sqrt{4\pi\lambda_o k_B T}} \quad \text{Eq. S1}$$

Case II) In the strong adiabatic, dynamic solvent effect controlled regime (DSE) with diffusive dynamics (high solvent friction, overdamped), the prefactor depends on the longitudinal solvent relaxation time  $\tau_L$ . For a cusped shape of the ground state free energy surface at the TS, which is appropriate for small coupling, one finds:

$$A_{\text{DSE}} = \frac{1}{\tau_L} \sqrt{\frac{\lambda_o}{16\pi k_B T}} \quad \text{Eq. S2}$$

Indeed, case I) yields for the MV compounds investigated in this work much too high rates for any reasonable combination of electronic coupling and reorganization energy. This is caused by an electronic coupling  $V$  which is too high to render the HT process diabatic. Likewise, case II) can be excluded as this applies to small couplings only.

### Calculation of the moment of inertia of nitrobenzene,<sup>1</sup> *ortho*-dichlorobenzene<sup>2</sup> and dichloromethane.<sup>3</sup>

For the calculation of the well frequency from the moment of inertia of the solvent we follow eq. 2 and A.4 in ref.<sup>4</sup> The moments of inertia for nitrobenzene are  $I_x = 652 \times 10^{-47}$  and  $I_y = 862 \times 10^{-47} \text{ kg m}^2$  which gives  $I_{\text{eff}} = 2 \left( \frac{1}{I_x} + \frac{1}{I_y} \right)^{-1} = 742 \times 10^{-47} \text{ kg m}^2$ . For *ortho*-dichlorobenzene  $I_x = 1011 \times 10^{-47}$  and  $I_y = 578 \times 10^{-47} \text{ kg m}^2$  gives  $I_{\text{eff}} = 736 \times 10^{-47} \text{ kg m}^2$ . For dichloromethane  $I_x = 26.2 \times 10^{-47}$  and  $I_y = 273.7 \times 10^{-47} \text{ kg m}^2$  gives  $I_{\text{eff}} = 48 \times 10^{-47} \text{ kg m}^2$ .

### Relaxation constants of PhNO<sub>2</sub>, oDCB and DCM.

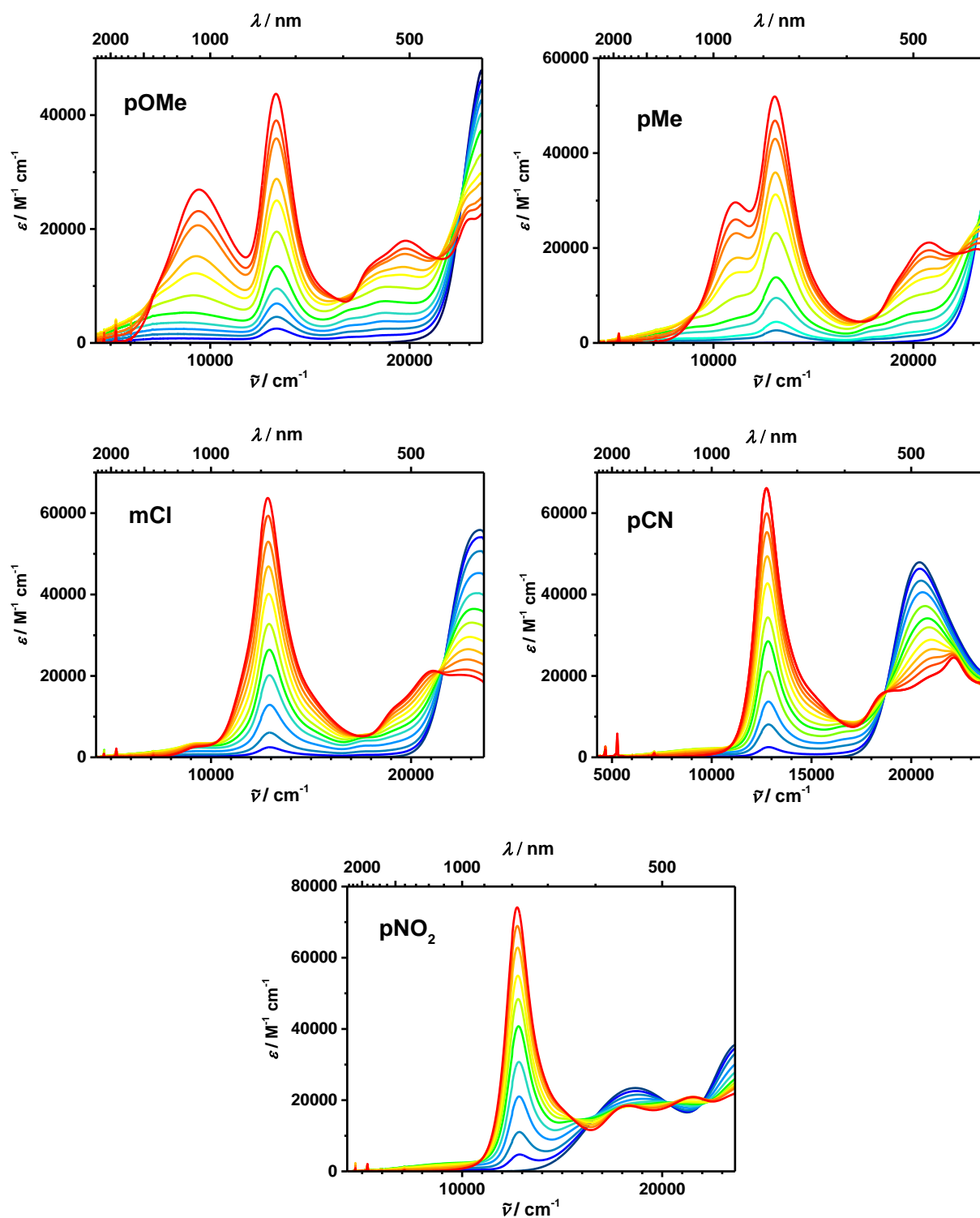
For the calculation of the longitudinal solvent relaxation constant  $\tau_L$  and the associated barrier we used the relation  $\tau_L = \frac{\epsilon_\infty}{\epsilon_s} \tau_D$ . For PhNO<sub>2</sub> the temperature dependent dielectric function ( $\tau_D, \epsilon_s, \epsilon_\infty$ ) was taken from ref.<sup>5</sup> The activation barrier  $H_L$  and  $\tau_0$  was obtained from the linear regression of  $\ln \tau_D = \ln \tau_0 + H_L/RT$  which gives  $\tau_0 = 3.55 \times 10^{-15} \text{ s}$  and  $H_L = 17.22 \text{ kJ mol}^{-1}$ . The Gibbs energy of activation given in ref.<sup>6</sup> agrees with this value ( $\Delta G^* = 14 \text{ kJ mol}^{-1}$  at rt). For oDCB it appears that no reliable temperature dependent dielectric data are available in literature. Ref.<sup>7</sup> presents the dielectric data for three different temperatures only. The data for rt agree with those from ref.<sup>8</sup>. Linear regression as above gives  $H_L = 7.3 \pm 1.6 \text{ kJ mol}^{-1}$  and  $\tau_0 = \ln(-28.8 \pm 0.6) \text{ s}$ . Although these values suggest a barrier that is significantly lower than that in PhNO<sub>2</sub> their accuracy, in particular of the

prefactor, is much too low to be useful for our purposes. For oDCB  $\tau_L$  at 298 K was estimated from  $\tau_D = 24.8 \text{ ps}$ <sup>8</sup>  $\epsilon_S = 9.93$  and  $\epsilon_\infty = n^2$  with  $n = 1.549$  to be 6.0 ps. The temperature dependence of these data appears not to be available for oDCB. However, according to standard theory the viscosity  $\eta$  should have a similar temperature dependence as the Debye relaxation time  $\tau_D$  which in turn has a similar temperature dependence as  $\tau_L$  provided that the dielectric permittivities  $\epsilon_S$  and  $\epsilon_\infty$  have negligible temperature dependence in the applied temperature range. For PhNO<sub>2</sub><sup>9</sup> a plot of  $\ln(\eta)$  with  $1/T$  displays a very good linear correlation with a barrier of 14.1 kJ mol<sup>-1</sup> which is somewhat smaller than the directly evaluated barrier above. For oDCB the viscosity is available at a number of temperatures<sup>10</sup> and the correlation yields a barrier of 10.6 kJ mol<sup>-1</sup>. Thus, for oDCB we reduced the rather precise  $H_L$  barrier of PhNO<sub>2</sub> (17.22 kJ mol<sup>-1</sup>) by the same factor by which the viscosity barrier of oDCB is smaller than that of PhNO<sub>2</sub> which gives  $H_L = 12.9 \text{ kJ mol}^{-1}$ . In order to obtain  $\tau_L = 6.0 \text{ ps}$  at 295 K the prefactor then must be  $3.11 \times 10^{-14} \text{ s}$ .

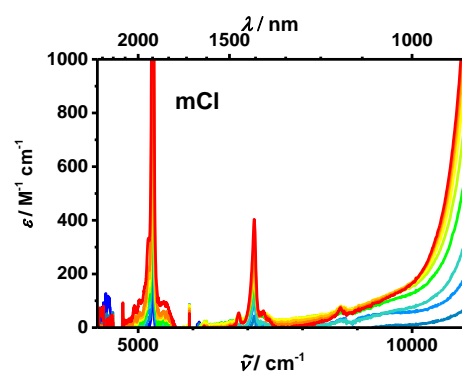
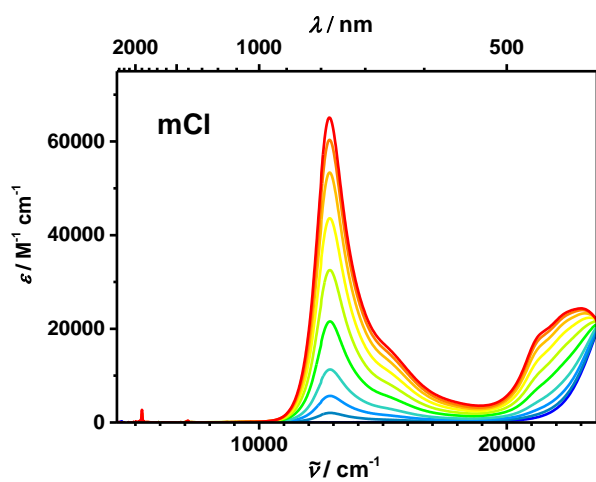
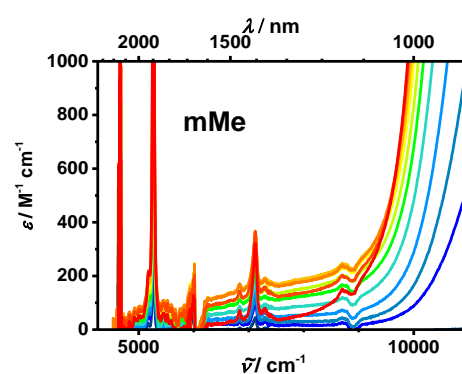
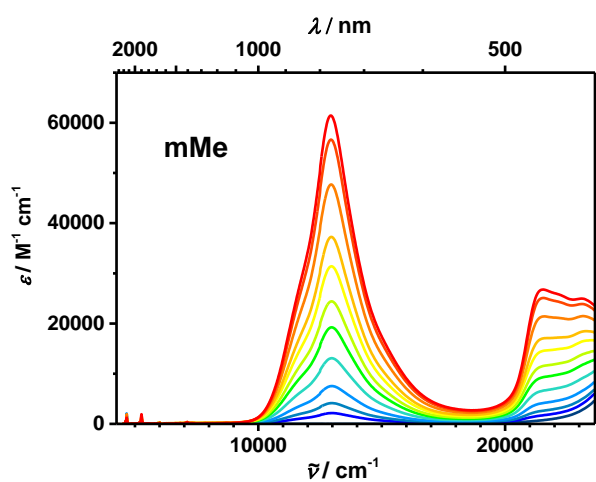
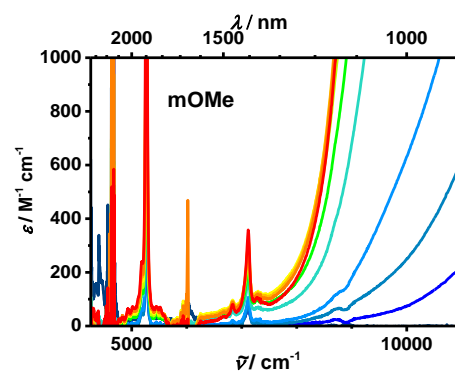
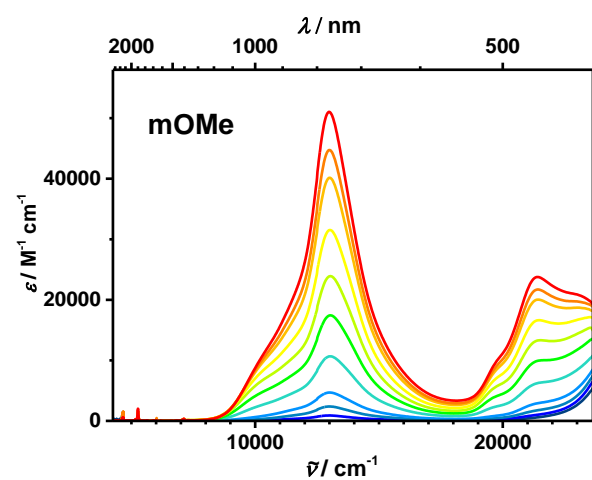
For DCM  $\tau_L$  at 298 K was estimated from  $\tau_D = 2.17 \text{ ps}$   $\epsilon_S = 8.83$  and  $\epsilon_\infty = 1.98$  to be 0.49 ps.<sup>11</sup> For DCM we again assume that the temperature dependence of the longitudinal relaxation time is the same as that of the Debye relaxation with  $H_L = 401 \text{ cm}^{-1}$  and  $\tau_0 = 7.05 \times 10^{-14} \text{ s}$ .<sup>11</sup>

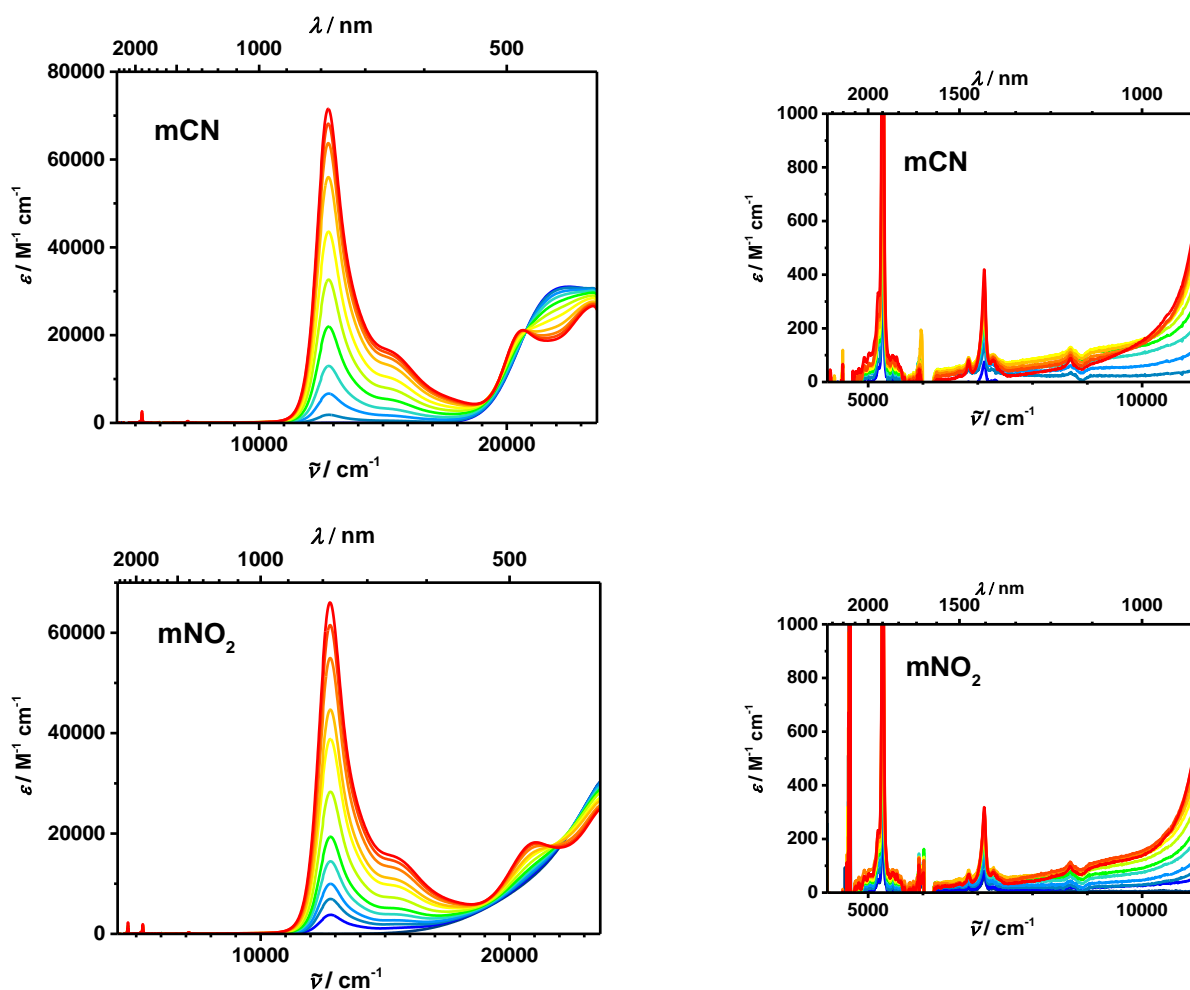
## Chemical Oxidation

Redox titrations monitored by UV/Vis/NIR spectroscopy were performed in three different solvents (PhNO<sub>2</sub>, oDCB and DCM) using a Cary 5000 UV-Vis-NIR absorption spectrometer (Agilent technologies) and 10×10 mm quartz-cuvettes with Teflon stopper (Hellma or Starna). PhNO<sub>2</sub> was distilled prior to use, oDCB (Acros) and DCM (Uvasol, Merck) were of spectroscopic grade and were used without further purification. SbCl<sub>5</sub> (Acros Organics) was used as oxidant in all cases. The bistriaryamine solution (ca. 1.5  $\mu\text{M}$ ) was titrated with a solution of SbCl<sub>5</sub> in the respective solvent (ca. 1 mM) using a microliter pipette (Eppendorf). The pure solvent was used as reference.

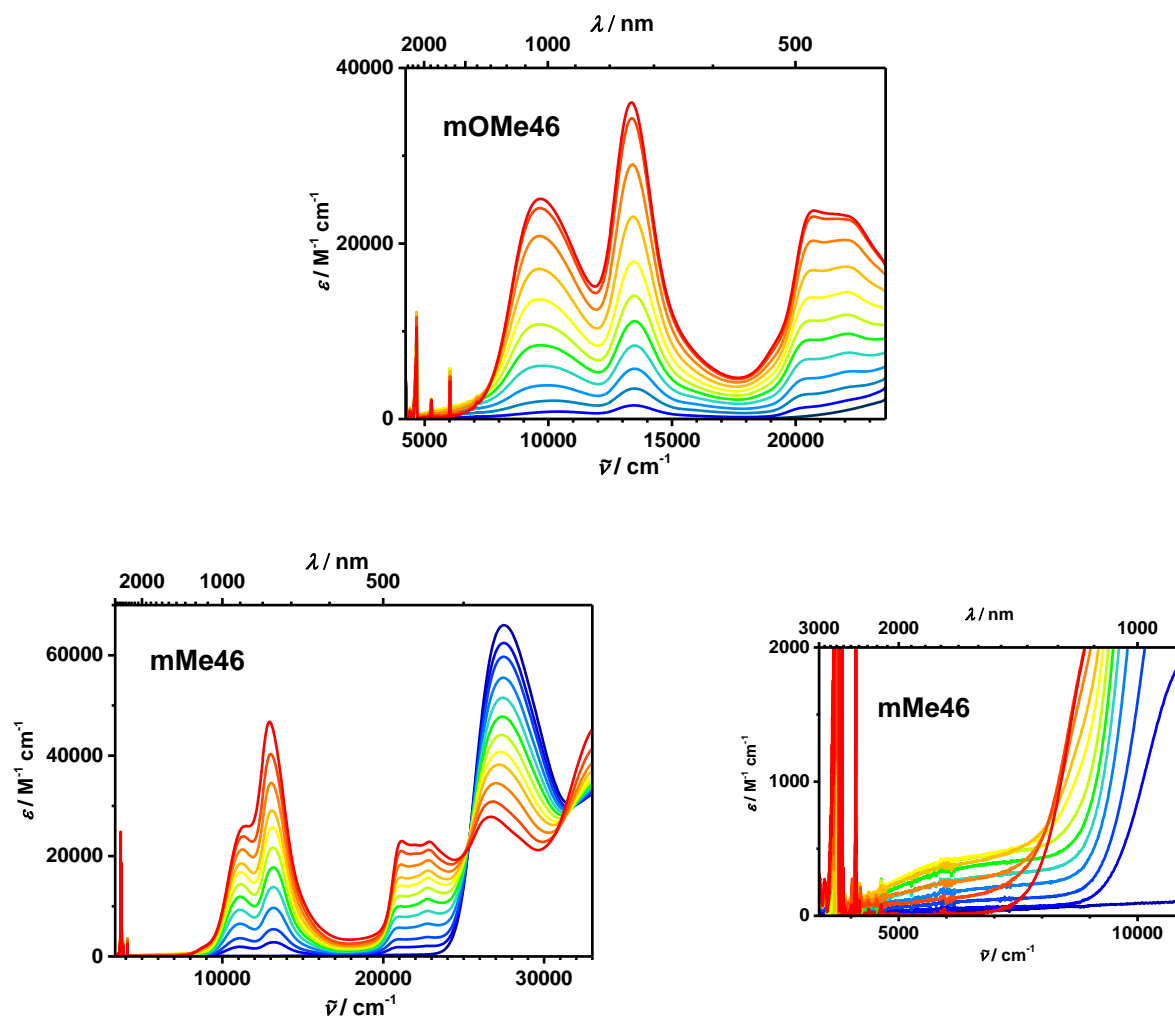


**Figure S1.** Absorption spectra of the *para*-compounds **pX** in  $\text{PhNO}_2$  (ca. 1.5  $\mu\text{M}$ ) while adding a solution of  $\text{SbCl}_5$  in  $\text{PhNO}_2$  (1 mM) dropwise. Sharp peaks in the NIR region are caused by residual overtone absorptions of the solvent and the oxidant.



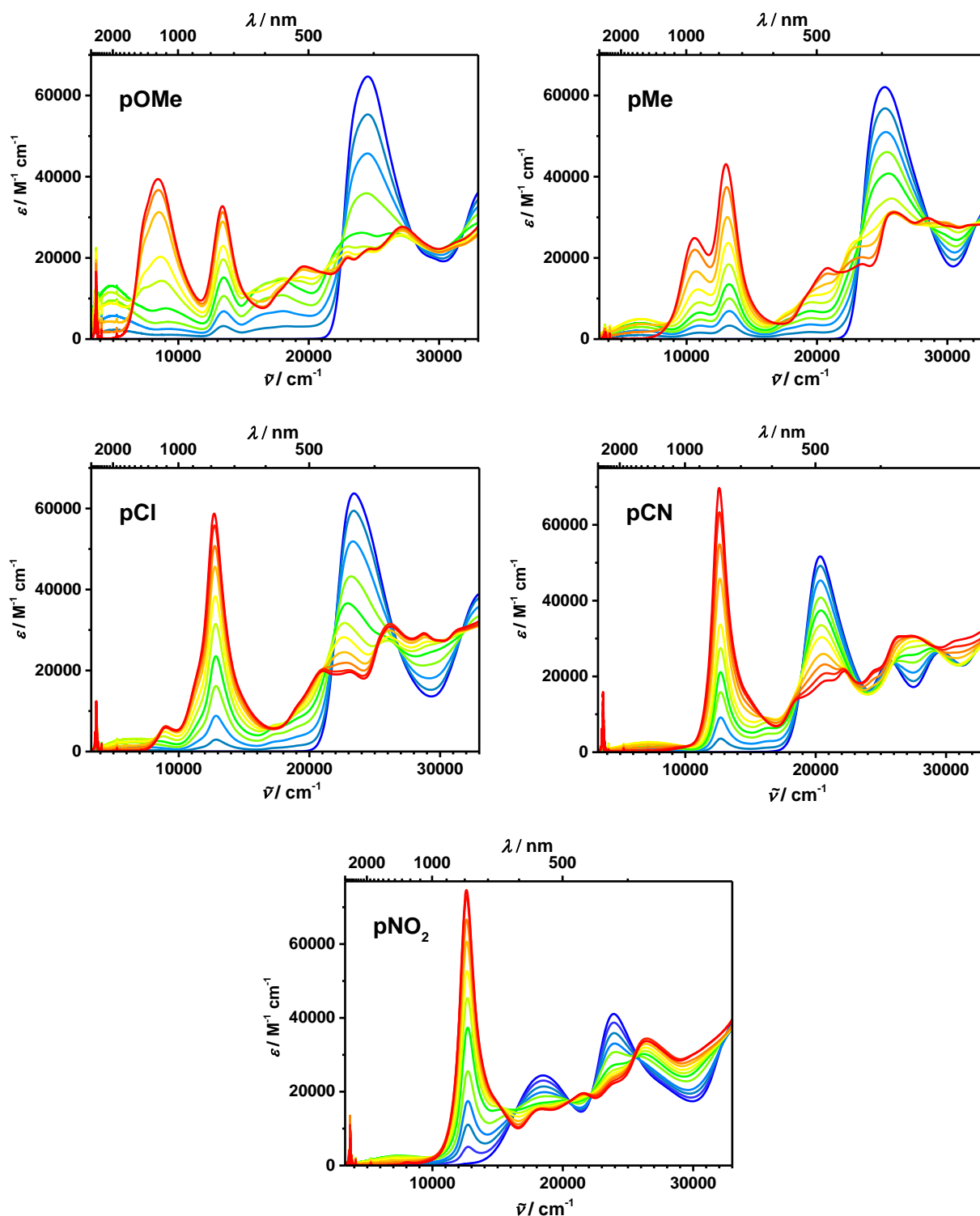


**Figure S2.** Absorption spectra of the *meta*-compounds **mX** in PhNO<sub>2</sub> (ca. 1.5  $\mu$ M) while adding a solution of SbCl<sub>5</sub> in PhNO<sub>2</sub> (1 mM) dropwise. The smaller figures on the right side show the magnified region where the IVCT-band is visible. Sharp peaks in the NIR region are caused by residual overtone absorptions of the solvent and the oxidant.



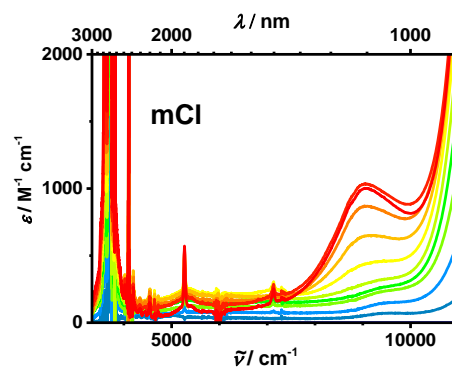
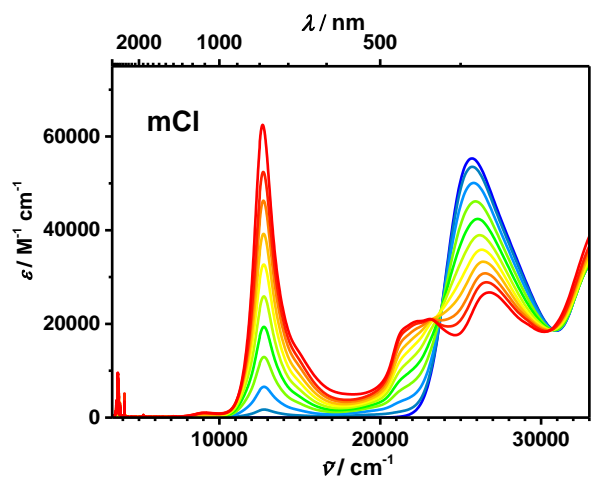
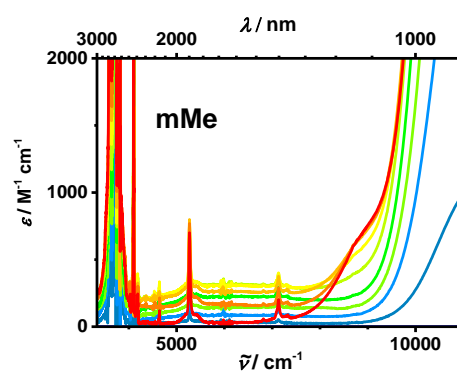
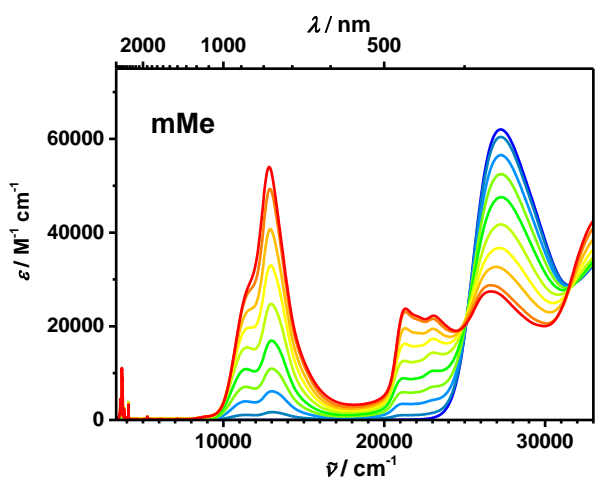
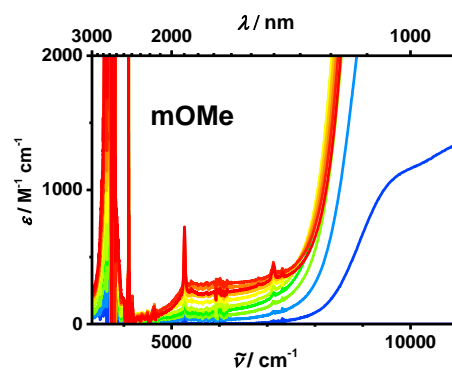
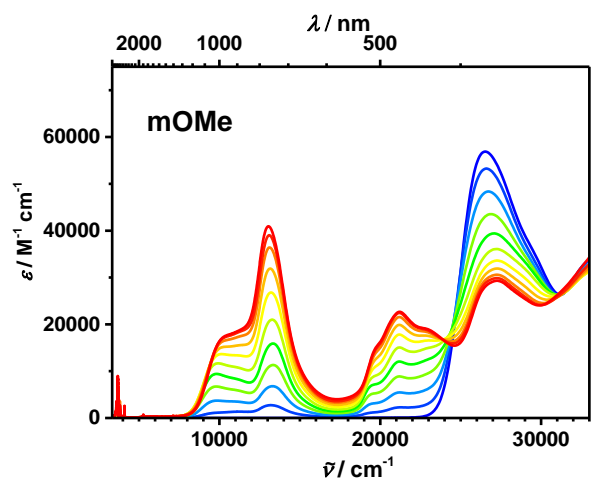
**Figure S3.** Absorption spectra of the *meta*-compounds **mOMe46** and **mMe46** in  $\text{PhNO}_2$  (ca. 1.5  $\mu\text{M}$ ) while adding a solution of  $\text{SbCl}_5$  in  $\text{PhNO}_2$  (1 mM) dropwise. Sharp peaks in the NIR region are caused by residual overtone absorptions of the solvent and the oxidant.

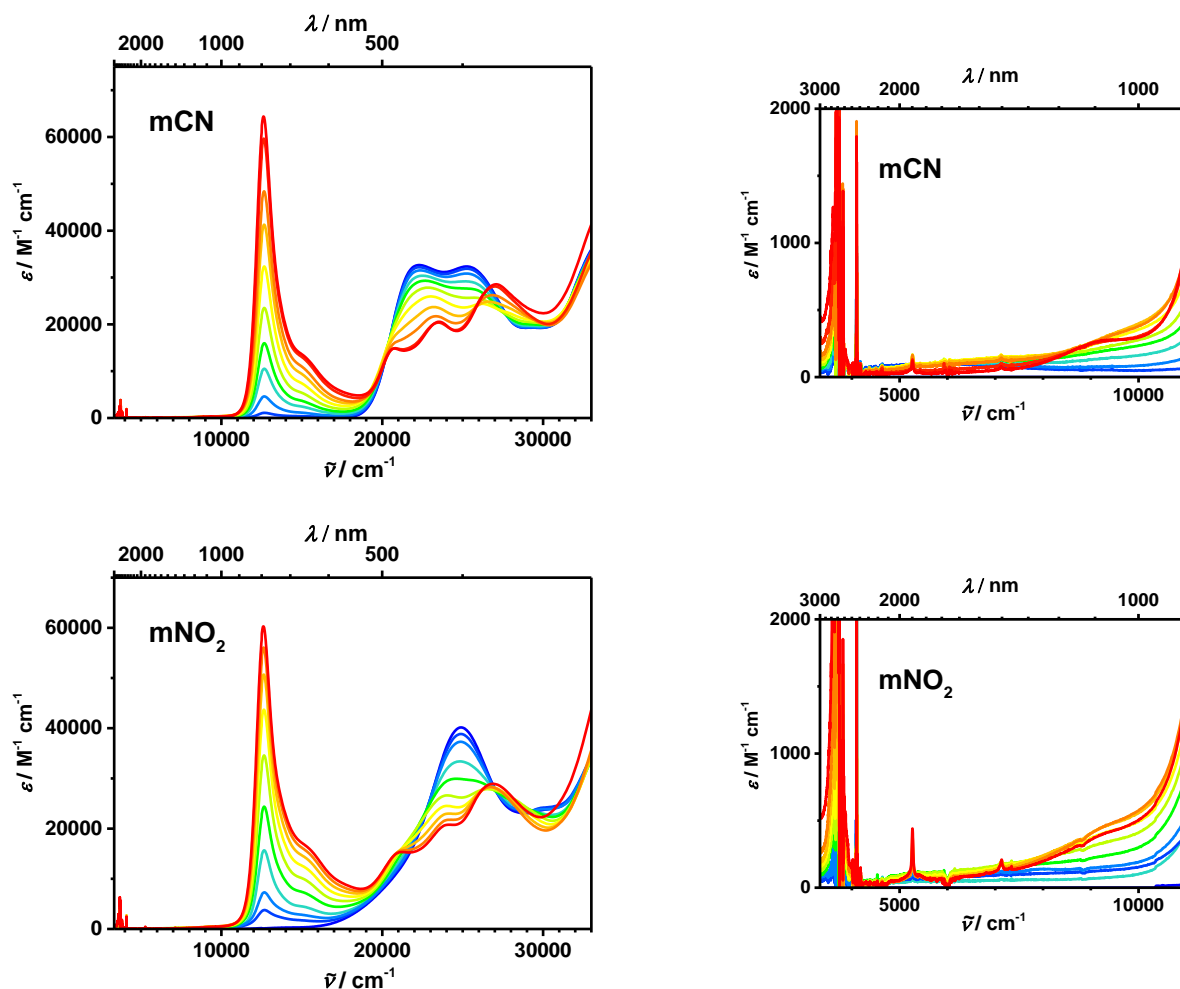
in oDCB



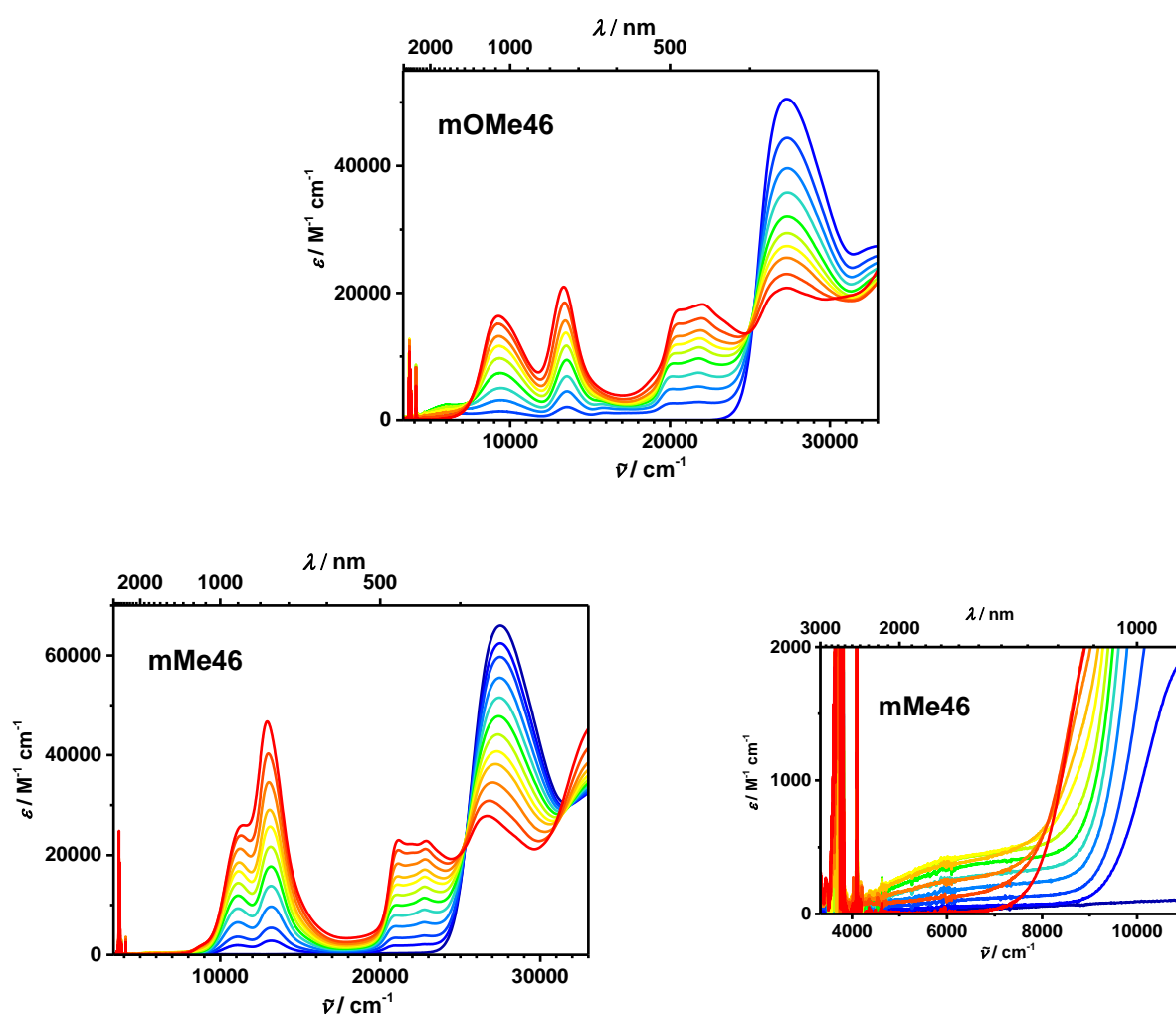
**Figure S4.** Absorption spectra of the *para*-compounds **pX** in oDCB (ca. 1.5  $\mu\text{M}$ ) while adding a solution of SbCl<sub>5</sub> in oDCB (1 mM) dropwise. Sharp peaks in the NIR region are caused by residual overtone absorptions of the solvent and the oxidant.



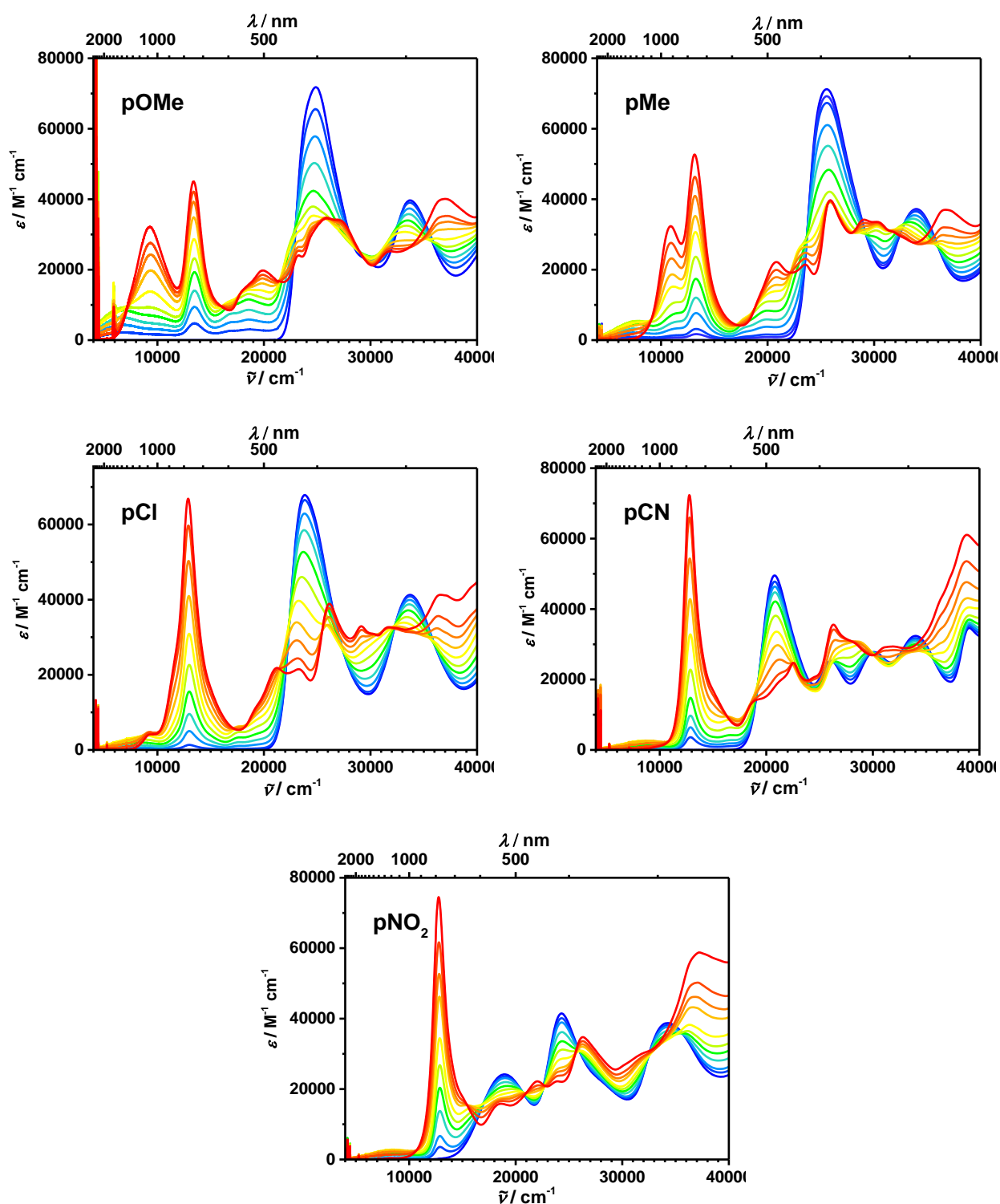




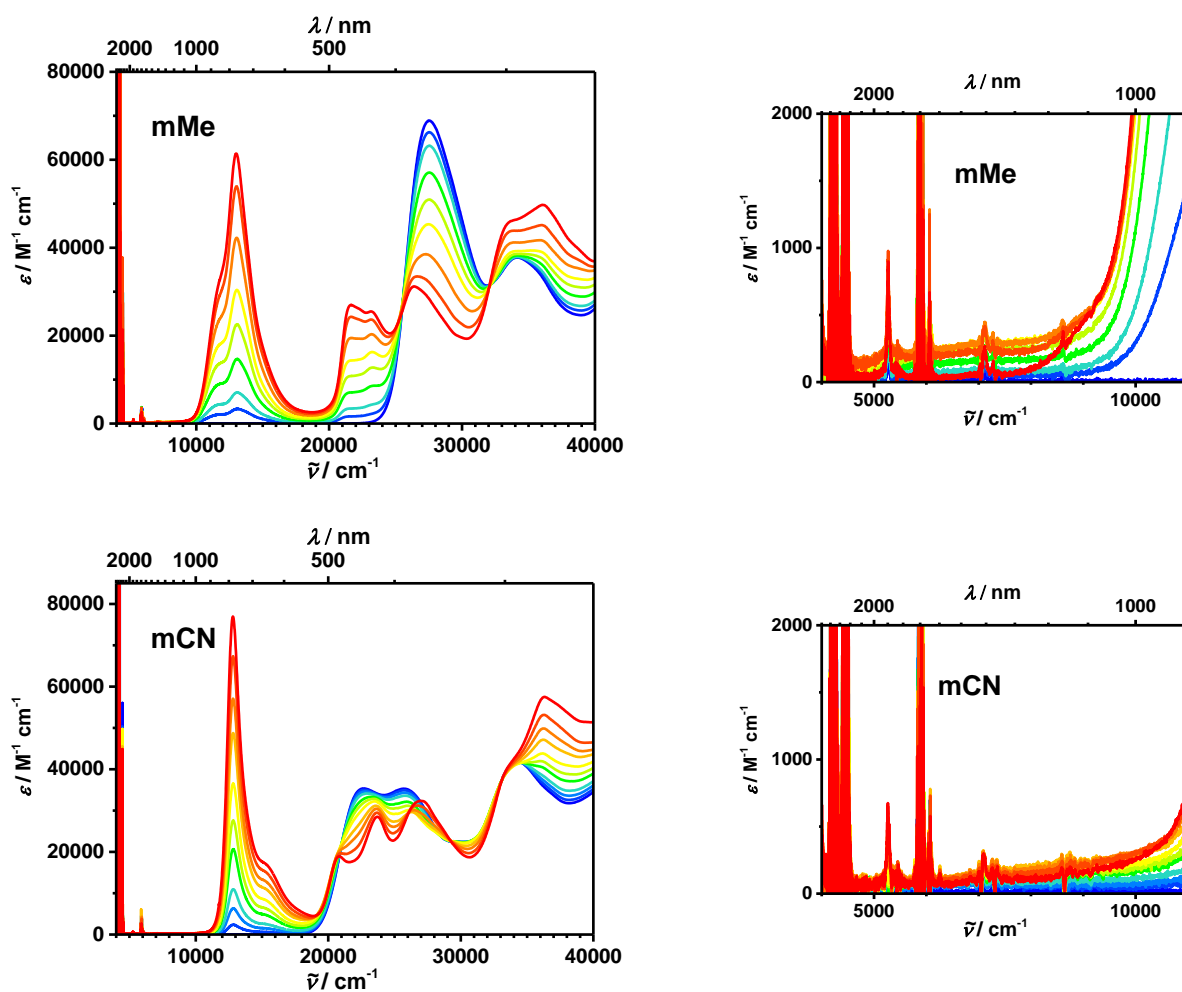
**Figure S5.** Absorption spectra of the *meta*-compounds **mX** in oDCB (ca. 1.5  $\mu\text{M}$ ) while adding a solution of  $\text{SbCl}_5$  in oDCB (1 mM) dropwise. The smaller figures on the right side show the magnified region where the IVCT-band is visible. Sharp peaks in the NIR region are caused by residual overtone absorptions of the solvent and the oxidant.



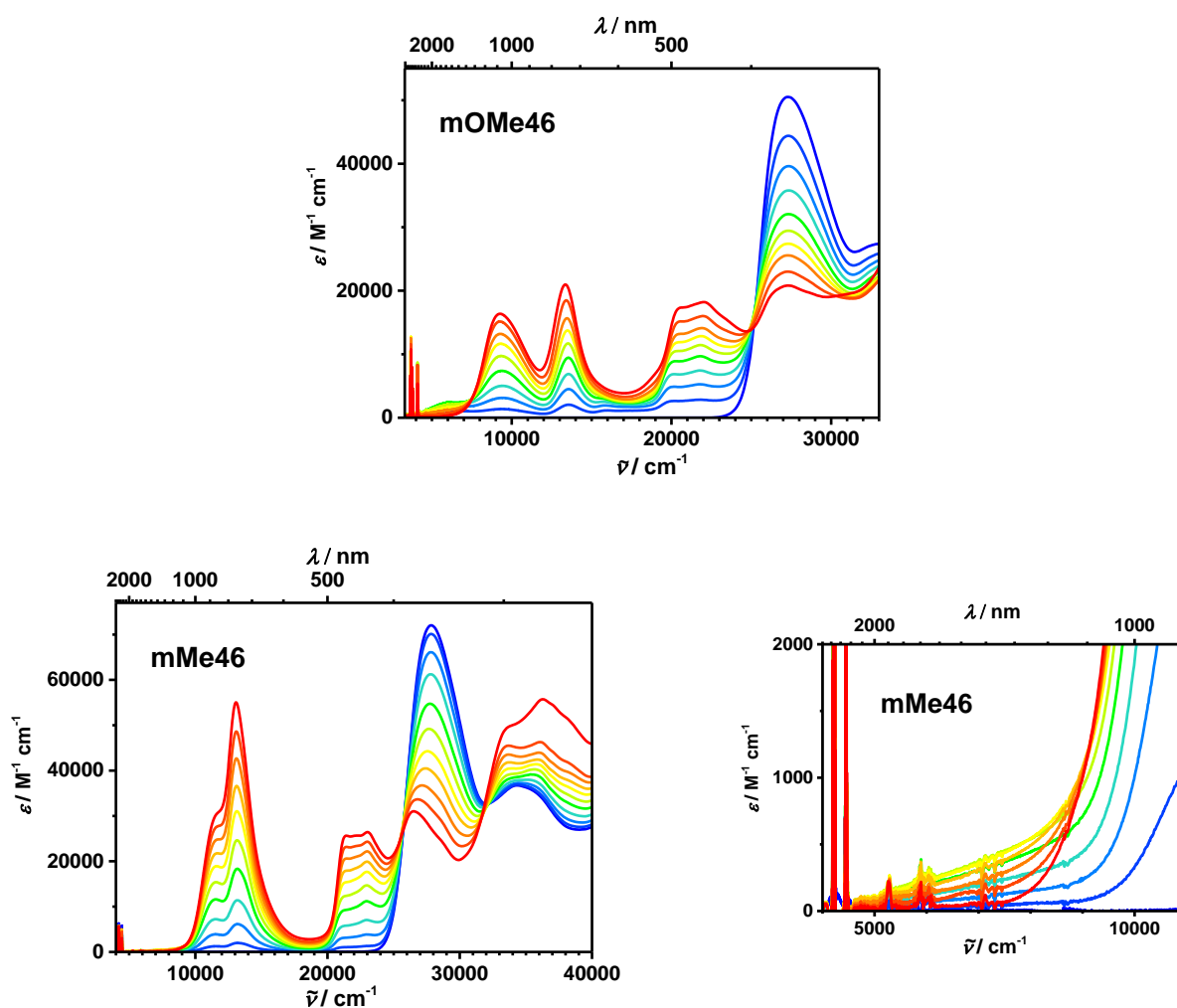
**Figure S6.** Absorption spectra of the *meta*-compound **mOMe46** and **mMe46** in oDCB (ca. 1.5  $\mu\text{M}$ ) while adding a solution of  $\text{SbCl}_5$  in oDCB (1 mM) dropwise. The smaller figures on the right side show the magnified region where the IVCT-band is visible. Sharp peaks in the NIR region are caused by residual overtone absorptions of the solvent and the oxidant.

in DCM

**Figure S7.** Absorption spectra of the *para*-compounds **pX** in DCM (ca. 1.5  $\mu\text{M}$ ) while adding a solution of SbCl<sub>5</sub> in DCM (1 mM) dropwise. Sharp peaks in the NIR region are caused by residual overtone absorptions of the solvent and the oxidant.

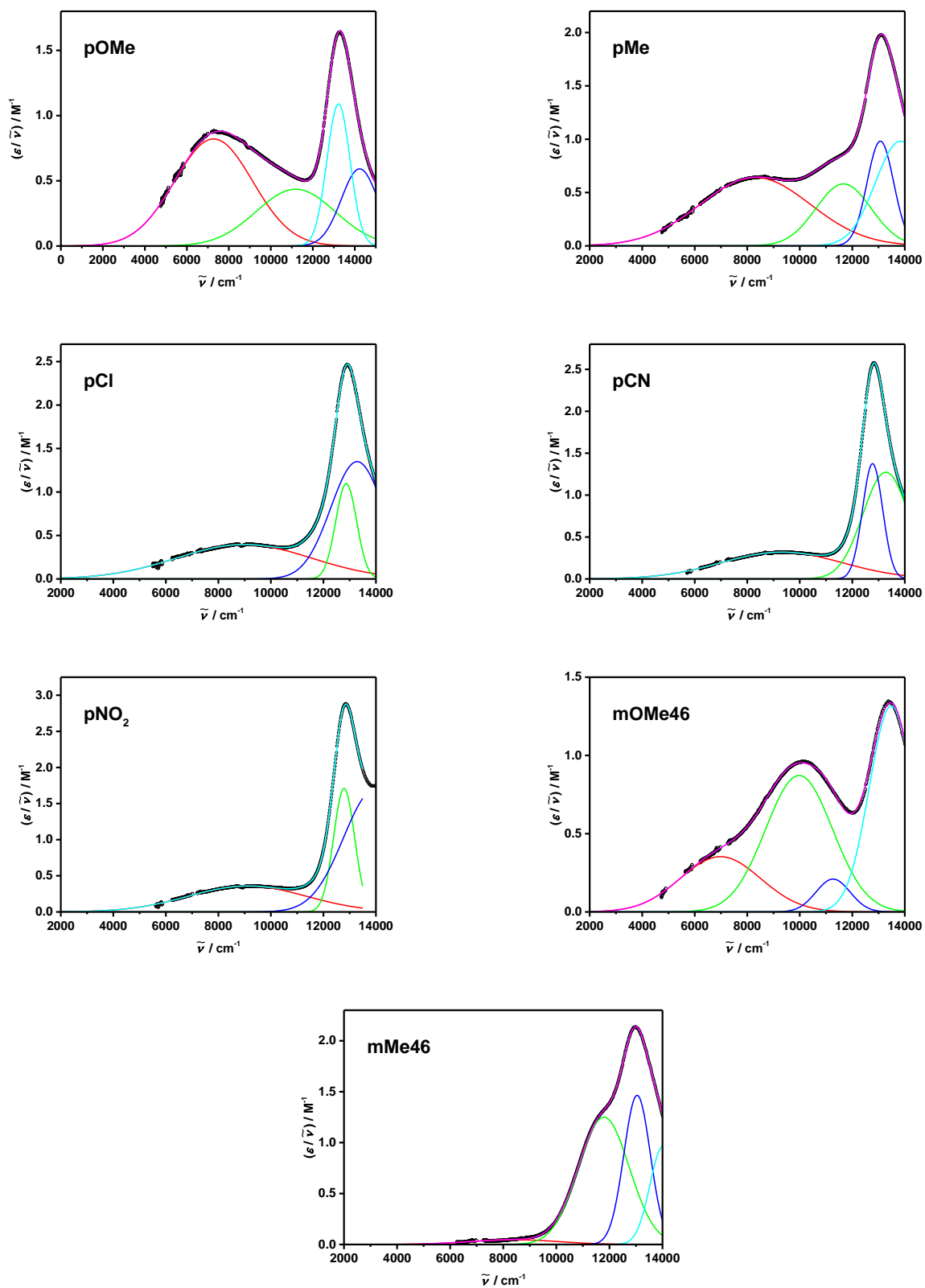


**Figure S8.** Absorption spectra of the *meta*-compounds **mMe** and **mCN** in DCM (ca. 1.5  $\mu\text{M}$ ) while adding a solution of  $\text{SbCl}_5$  in DCM (1 mM) dropwise. The smaller figures on the right side show the magnified region where the IVCT-band is visible. Sharp peaks in the NIR region are caused by residual overtone absorptions of the solvent and the oxidant.



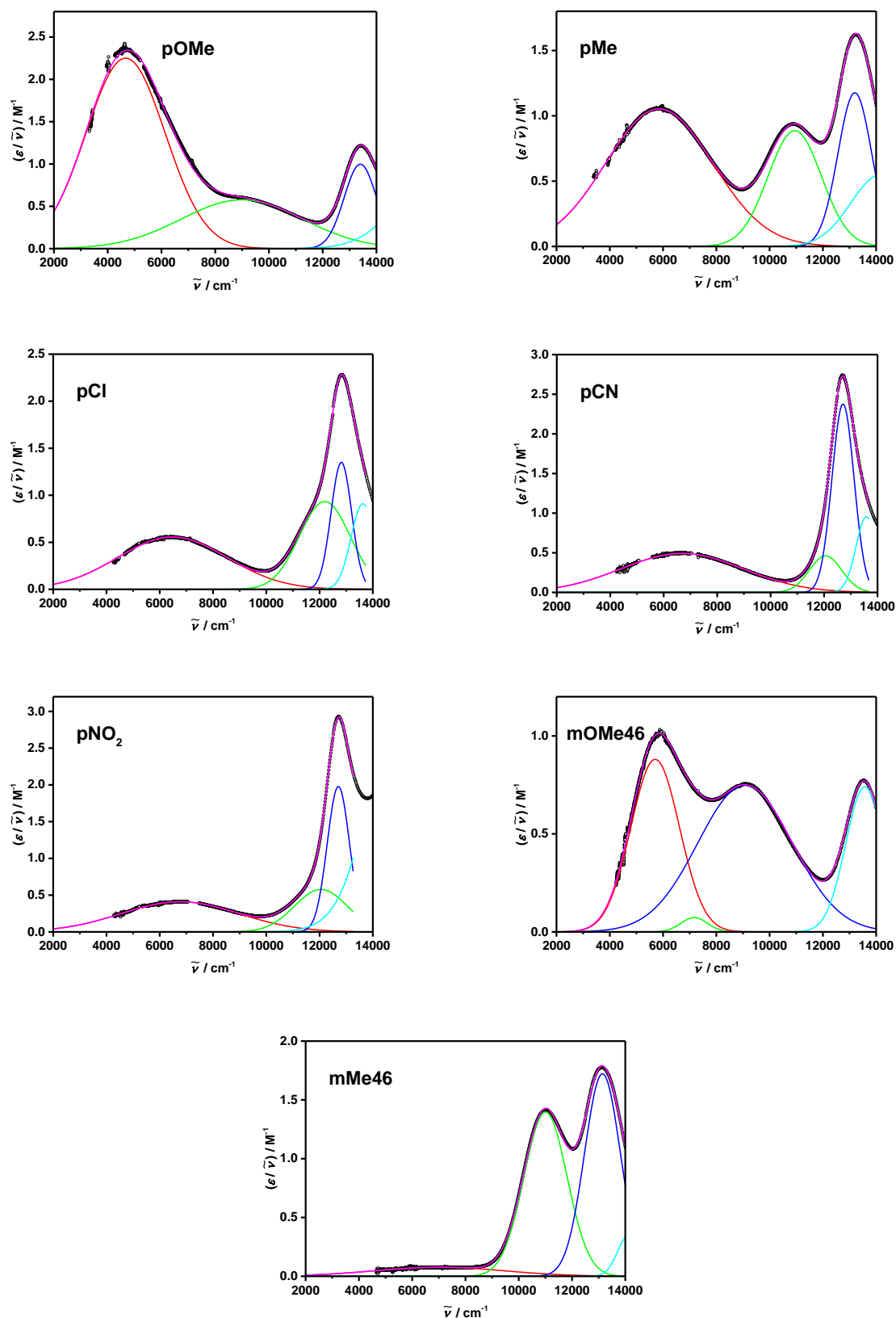
**Figure S9.** Absorption spectra of the *meta*-compound **mOMe46** and **mMe46** in DCM (ca. 1.5  $\mu\text{M}$ ) while adding a solution of  $\text{SbCl}_5$  in DCM (1 mM) dropwise. The smaller figures on the right side show the magnified region where the IVCT-band is visible. Sharp peaks in the NIR region are caused by residual overtone absorptions of the solvent and the oxidant.

For all compounds **pX**, **mOMe46** and **mMe46** the monocation spectra were calculated assuming that the monocation band at ca. 14000 cm<sup>-1</sup> possesses half the height of the dication band which is a good approximation if the interaction of the triarylamines is weak. Thus, the redox titration was performed to a point where all chromophores were oxidized to the dication and no further change of spectra was observed upon further addition of oxidant. The extinction coefficient of the dication band at 14000 cm<sup>-1</sup> was divided by 2 to yield  $\varepsilon_{\max}^+$  of the monocation ( $\varepsilon_{\max}^+ = \frac{\varepsilon_{\max}^{2+}}{2}$ ). For the construction of the “pure” monoradical spectrum we used a spectrum recorded at very little addition of oxidant where only insignificant amounts of dication are present because of the comproportionation equilibrium. This spectrum with extinction coefficient  $\varepsilon^+$  at ca. 14000 cm<sup>-1</sup> was then multiplied by a factor  $f = \frac{\varepsilon_{\max}^+}{\varepsilon^+}$  in order to obtain the true monocation spectrum. For extracting the IV-CT band the reduced spectra ( $\varepsilon/\tilde{\nu}$ ) of the monoradical cation were then fitted with up to four Gaussian functions as given in Figures S10-S12.

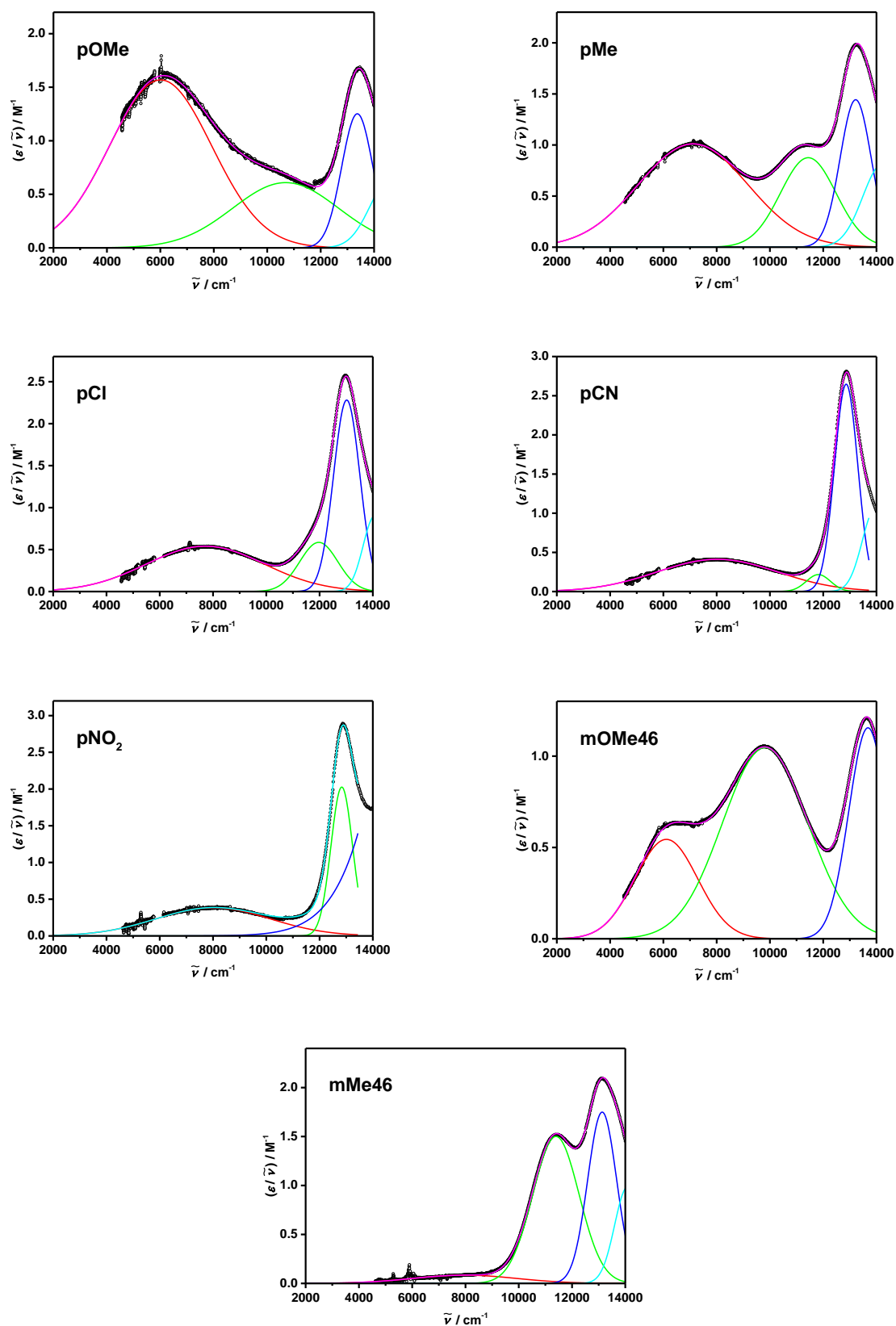


**Figure S10.** Reduced absorption spectra of **pX**, **mOMe46** and **mMe46** in  $\text{PhNO}_2$  and fit with Gaussian functions. The IV-CT band is given in red.

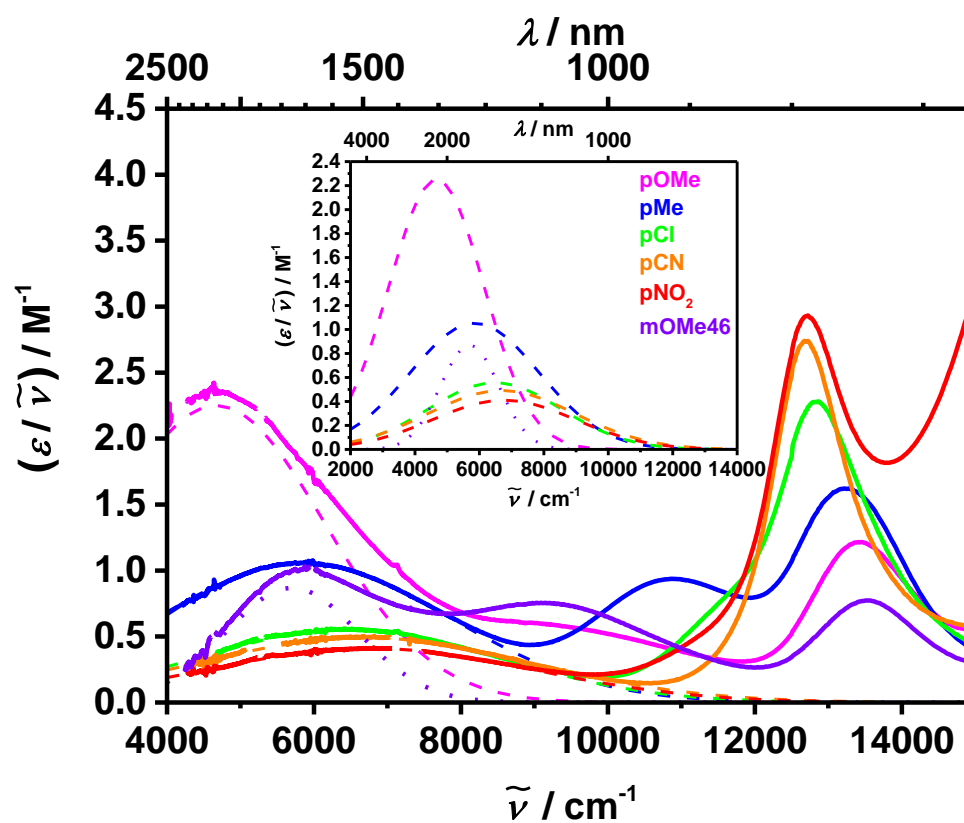




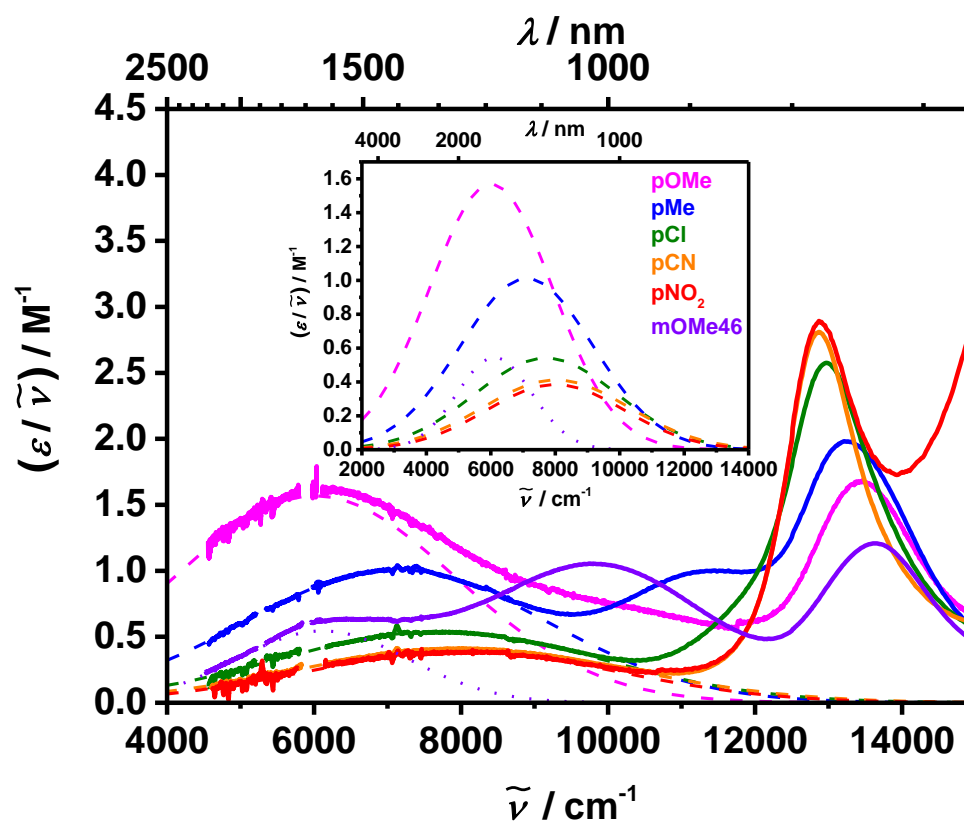
**Figure S11.** Reduced absorption spectra of the monocation of **pX**, **mOMe46** and **mMe46** in oDCB and fit with Gaussian functions. The IV-CT band is given in red.



**Figure S12.** Reduced absorption spectra of the monocation of **pX**, **mOMe46** and **mMe46** in DCM and fit with Gaussian functions. The IV-CT band is given in red.



**Figure S13.** Reduced absorption spectra of the monocations of **pX** and of **mOMe46** in oDCB and fit with Gaussian functions magnified in the inset.

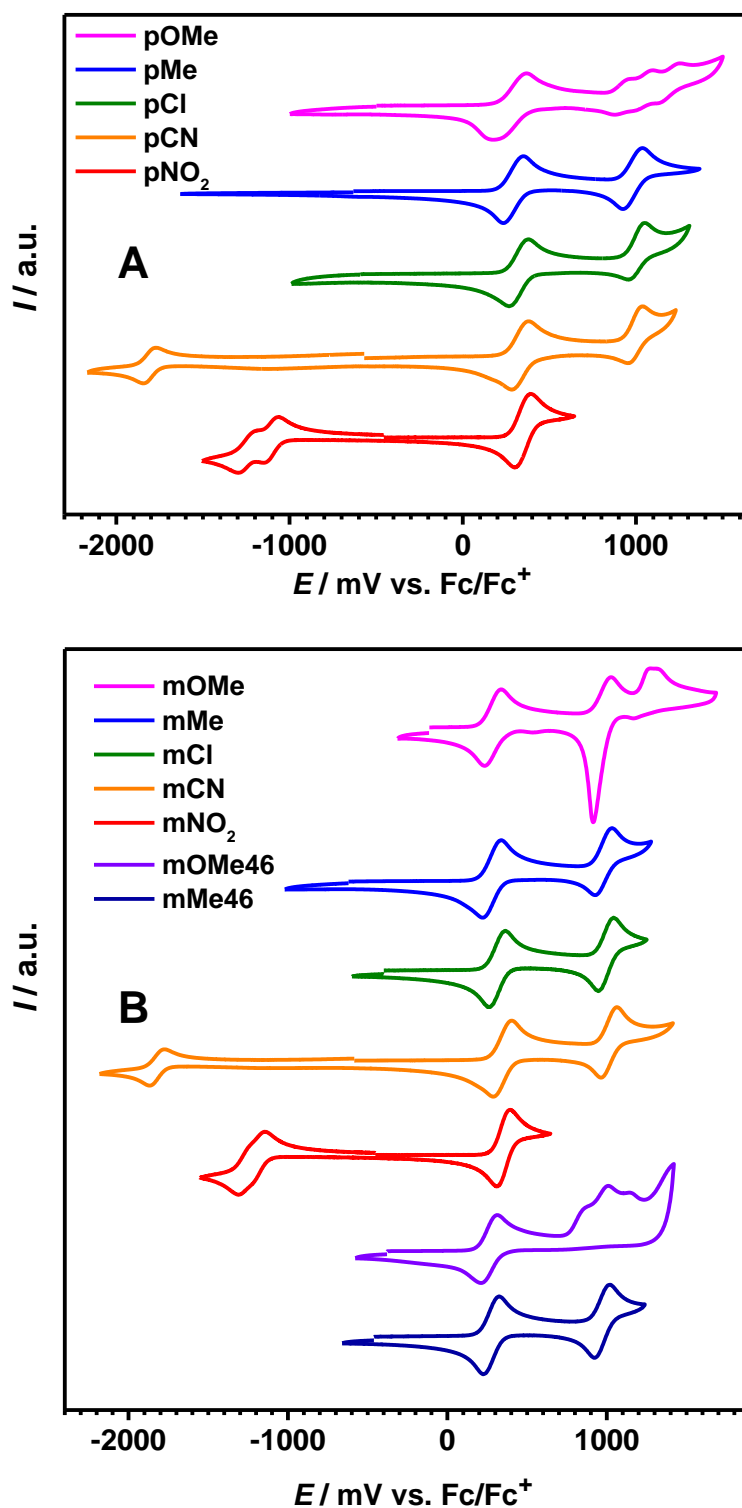


**Figure S14.** Reduced absorption spectra of the monocations of **pX** and of **mOMe46** in DCM and fit with Gaussian functions magnified in the inset.

### **Cyclic Voltammetry (CV), Squarewave Voltammetry (SWV) and Differential Pulse Voltammetry (DPV)**

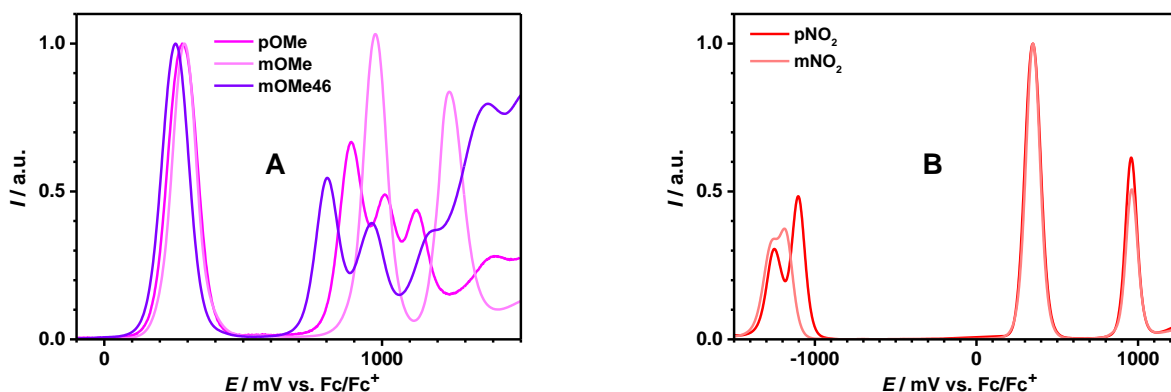
The electrochemical measurements were performed with a Gamry Instruments Reference 600 Potentiostat/Galvanostat/ZRA (v. 6.2.2, Warminster, PA, USA). The cyclic voltammograms of all compounds (2 mM) were measured under an argon atmosphere in DCM with tetrabutylammonium hexafluorophosphate (TBAHF, 0.2 M) as conducting salt. A conventional three electrode set-up consisting of a platinum disc working electrode ( $\varnothing = 1$  mm), a Ag/AgCl 'LEAK FREE' reference electrode (Warner Instruments, Hamden, CT, USA) and a platinum wire counter electrode was used. The measurement cell was dried in an oven and flushed with argon before use. The reference electrode was referenced against the ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox couple. Chemical and electrochemical reversibility (referring to the absence of chemical follow up reactions and the reversability of the heterogenous electron transfer processes at the electrode, respectively) of the redox processes particularly around 300 mV were checked by multi thin layer experiments<sup>12</sup> and measurements at different scan rates (from 25–1000  $\text{mV s}^{-1}$ ), respectively.

In all cases the CV signals at ca. 300 mV cover two redox processes associated with the first oxidation of each triarylamine group (see Fig. 4). The electrostatic interaction is so weak that these two processes do not appear as separated waves in the CV.<sup>13</sup> The signals at ca. 1000 mV also cover two redox processes and refer to the second oxidation of each triarylamine. In case of the methoxy substituted derivatives in this potential region there are also redox processes associated with the bridge as can be seen by the SWV and DPV in Fig. S16.



**Figure S15.** A: Cyclic voltammograms of the *para*-compounds **pX**. B: Cyclic voltammograms of the *meta*-compounds **mX**. The voltammograms of all compounds were

recorded in DCM/0.2 M TBAHF at a scan rate of  $1000 \text{ mV s}^{-1}$ . The **NO<sub>2</sub>** compounds were recorded at a scan rate of  $100 \text{ mV s}^{-1}$ .

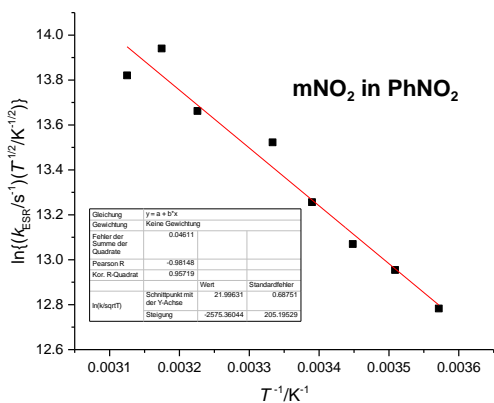
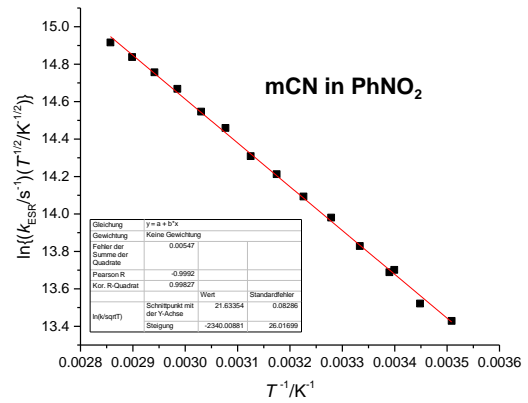
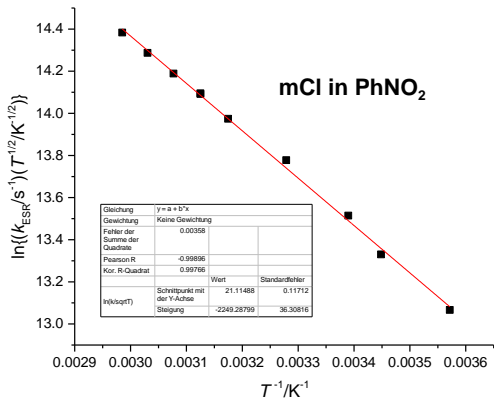
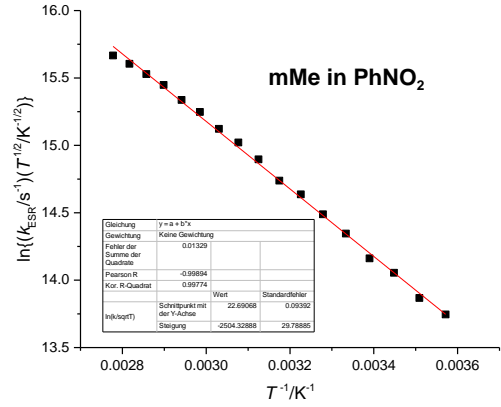
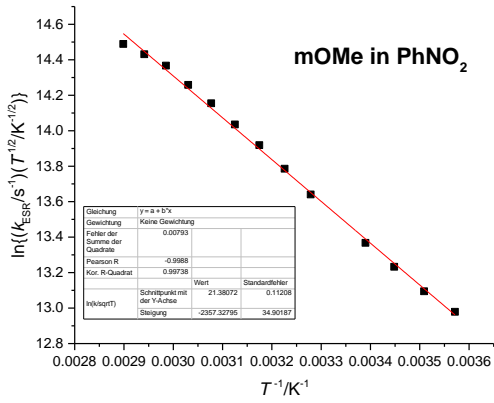


**Figure S16.** **A:** Squarewave voltammogram of **p/mOMe** and **mOMe46** in DCM at a scan rate of  $50 \text{ mV s}^{-1}$ . **B:** Differential pulse voltammetry of **pNO<sub>2</sub>** and **mNO<sub>2</sub>** in DCM at a scan rate of  $2 \text{ mV s}^{-1}$ .

**Table S1.** Redox potentials of the bistriarylamines in DCM/0.2 M TBAHF.<sup>d</sup>

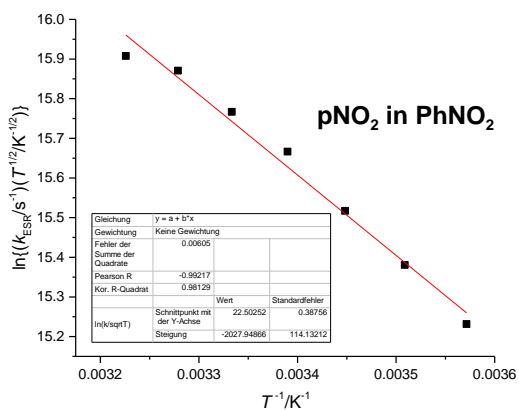
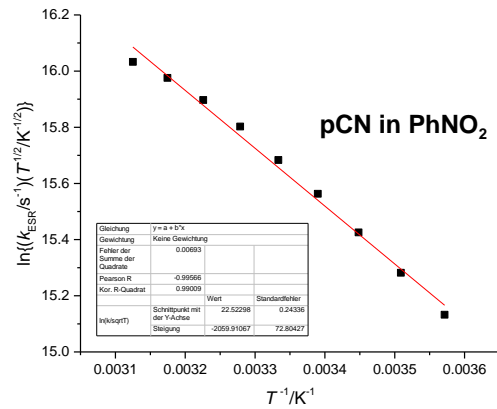
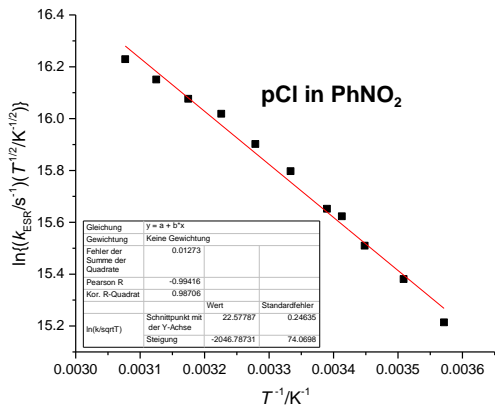
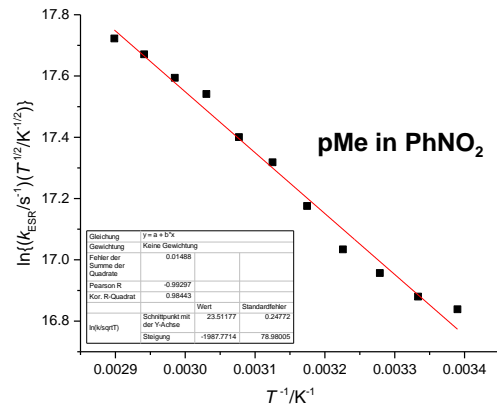
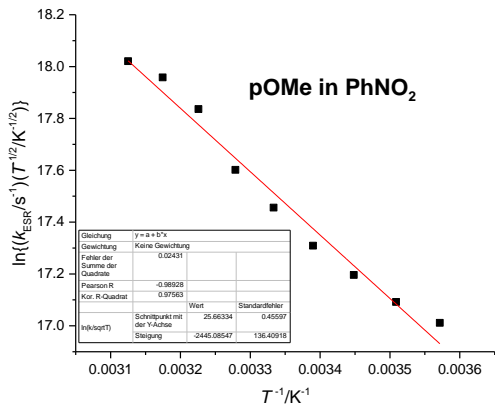
	$E_{1/2}(\text{Red2})$	$E_{1/2}(\text{Red1})$	$E_{1/2}(\text{Ox1})$	$E_{1/2}(\text{Ox2})^a$	$E_{1/2}(\text{Ox3})^a$	$E_{1/2}(\text{Ox4})^a$	$E_{1/2}(\text{Ox5})^a$
	/ mV	/ mV	/ mV	/ mV	/ mV	/ mV	/ mV
<b>pOMe</b>	-	-	<b>280</b>	884 <sup>b</sup>	1004 <sup>b</sup>	1120 <sup>b</sup>	1404 <sup>b</sup>
<b>pMe</b>	-	-	<b>292</b>	982	-	-	-
<b>pCl</b>	-	-	<b>321</b>	1004	-	-	-
<b>pCN</b>	-	-1787 <sup>a</sup>	<b>343</b>	1000	-	-	-
<b>pNO<sub>2</sub></b>	-1249 <sup>c</sup>	-1103 <sup>c</sup>	<b>345</b>	957 <sup>c</sup>	-	-	-
<b>mOMe</b>	-	-	<b>287</b>	976 <sup>b</sup>	-	-	-
<b>mMe</b>	-	-	<b>280</b>	979	-	-	-
<b>mCl</b>	-	-	<b>313</b>	998	-	-	-
<b>mCN</b>	-	-1799 <sup>a</sup>	<b>348</b>	1011	-	-	-
<b>mNO<sub>2</sub></b>	-1287 <sup>c</sup>	-1186 <sup>c</sup>	<b>349</b>	966 <sup>c</sup>	-	-	-
<b>mOMe46</b>	-	-	<b>256</b>	804	964 <sup>b</sup>	1183 <sup>b</sup>	1379 <sup>b</sup>
<b>mMe46</b>	-	-	<b>275</b>	969	-	-	-

<sup>a</sup>Irreversible process. <sup>b</sup>Value determined by SWV. <sup>c</sup>Value determined by DPV. <sup>d</sup> $\pm 5 \text{ mV}$

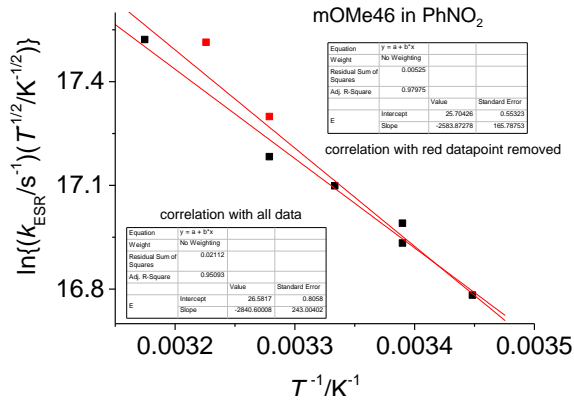
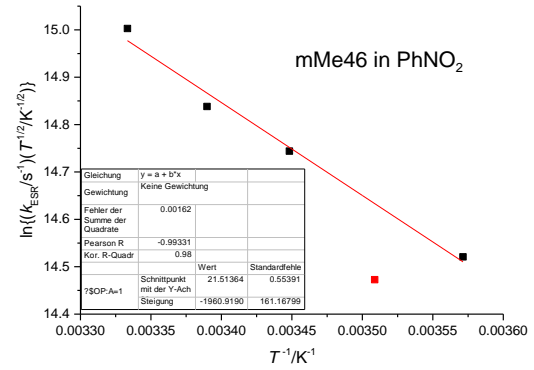
mX in PhNO<sub>2</sub>:

**S17a.**  $\ln(k/T^{1/2})$  vs  $1/T$  plots for all compounds in PhNO<sub>2</sub>, oDCB and DCM.

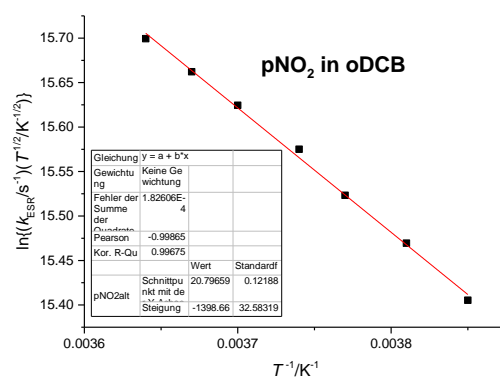
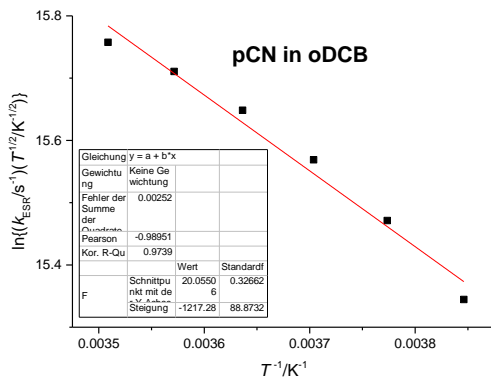
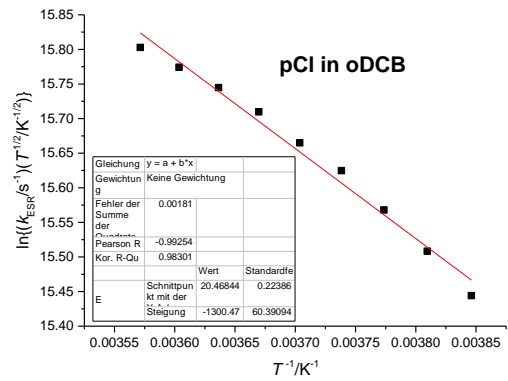
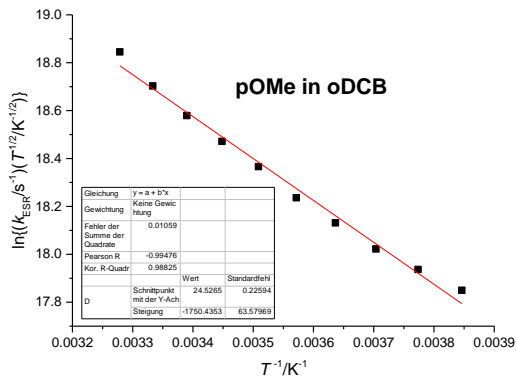


pX in PhNO<sub>2</sub>

**S17b.**  $\ln(k/T^{1/2})$  vs  $1/T$  plots for all compounds in PhNO<sub>2</sub>, oDCB and DCM.

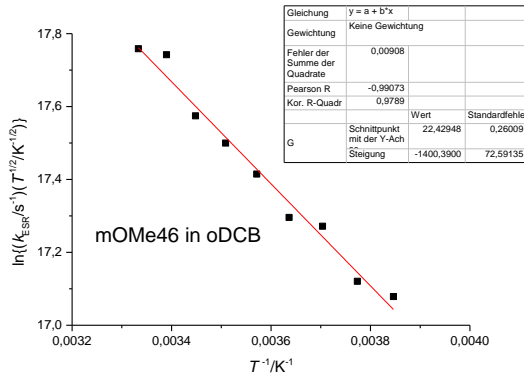
mOMe46 in PhNO<sub>2</sub>:mMe46 in PhNO<sub>2</sub>:

## pX in oDCB

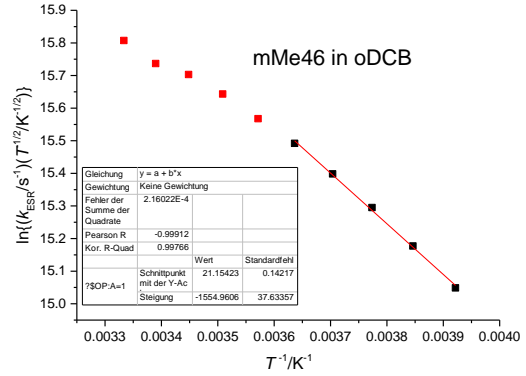


**S17c.**  $\ln(k/T^{1/2})$  vs  $1/T$  plots for all compounds in PhNO<sub>2</sub>, oDCB and DCM.

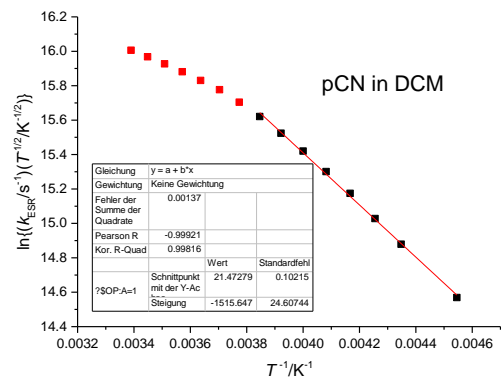
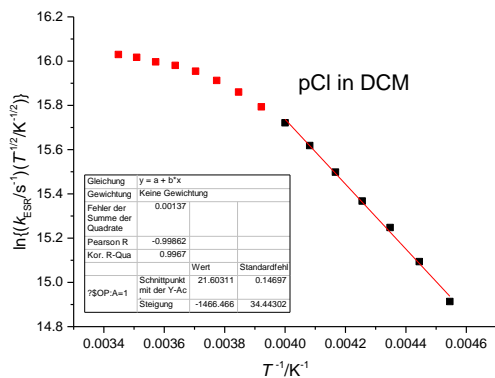
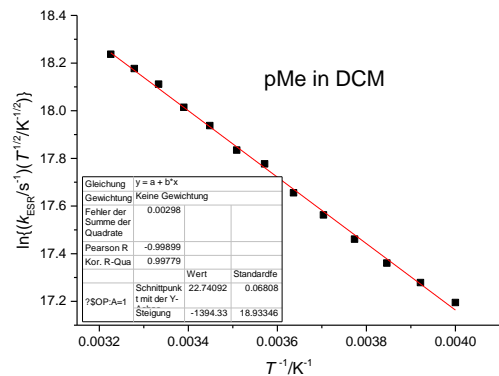
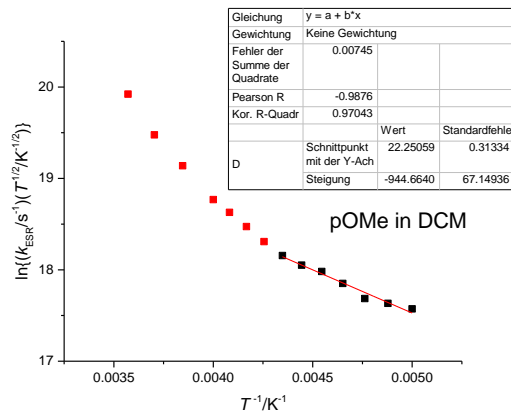
## mOMe46 in oDCB:



## mMe46 in oDCB:

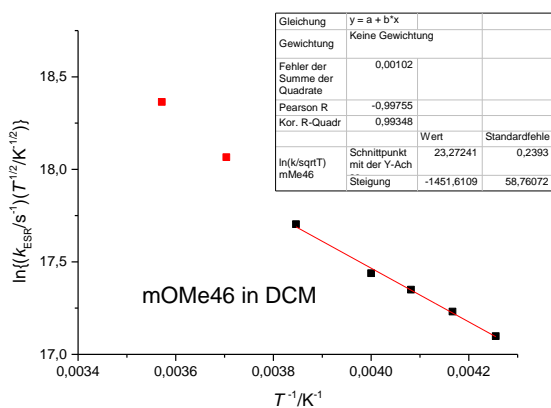


## pX in DCM:

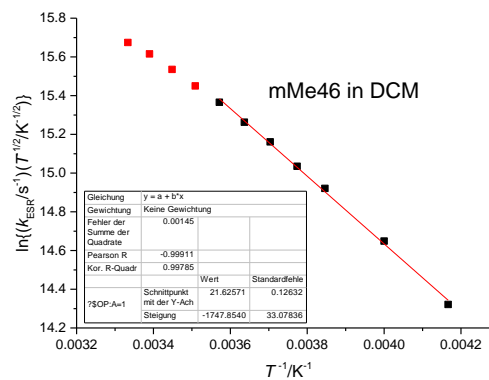


**S17d.**  $\ln(k/T^{1/2})$  vs  $1/T$  plots for all compounds in PhNO<sub>2</sub>, oDCB and DCM.

mOMe46 in DCM:



mMe46 in DCM:



**S17e.**  $\ln(k/T^{1/2})$  vs  $1/T$  plots for all compounds in  $\text{PhNO}_2$ , oDCB and DCM.

## Synthesis

Commercially available compounds including solvents were purchased from Fluka, Sigma-Aldrich, Merck, Acros or Chempur and used without further purification.

All reactions specified as being performed under nitrogen atmosphere were performed in air-free conditions (nitrogen, dried with Sicapent® from Merck, oxygen was removed by copper oxide catalyst R3-11 from BASF) using solvents freshly dried and deoxygenated by standard procedures.

Flash column chromatography was performed on standard silica gel, 60 Å, 40–63 µm (Merck). Preparative size exclusion gel permeation chromatography was performed with two sequential columns 10 µm, 50 Å and 500 Å (PSS) in a recycling set-up.

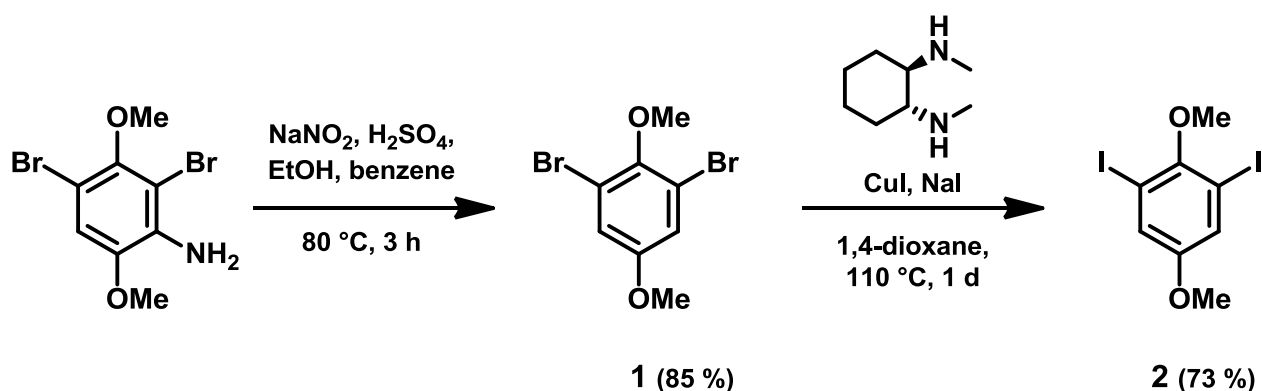
Proton and carbon nuclear magnetic resonance spectra were measured on an Avance III HD 400 FT-Spectrometer (<sup>1</sup>H: 400.13 MHz, <sup>13</sup>C: 100.61 MHz) and an Avance III HD 600 FT-Spectrometer (<sup>1</sup>H: 600.13 MHz, <sup>13</sup>C: 150.90 MHz). The residual signal of the respective solvent was used as the internal reference and the chemical shifts are given in ppm (δ-scale). The proton signals are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet. The carbon signals are abbreviated as follows: CH<sub>3</sub> = primary, CH<sub>2</sub> = secondary, CH = tertiary, C<sub>q</sub> = quaternary. Multiplet signals or overlapping signals in proton NMR spectra that could not be assigned to first order couplings are given as (-).

Mass spectrometry was performed on a Finnigan MAT 90 (EI) or with a Bruker Daltonic microTOF focus (ESI). All mass spectrometry peaks are reported as m/z. For calculation of the respective mass values of the isotopic distribution, the software module "Bruker Daltonics IsotopePattern" from the software Compass 1.1 from Bruker Daltonics GmbH was used.

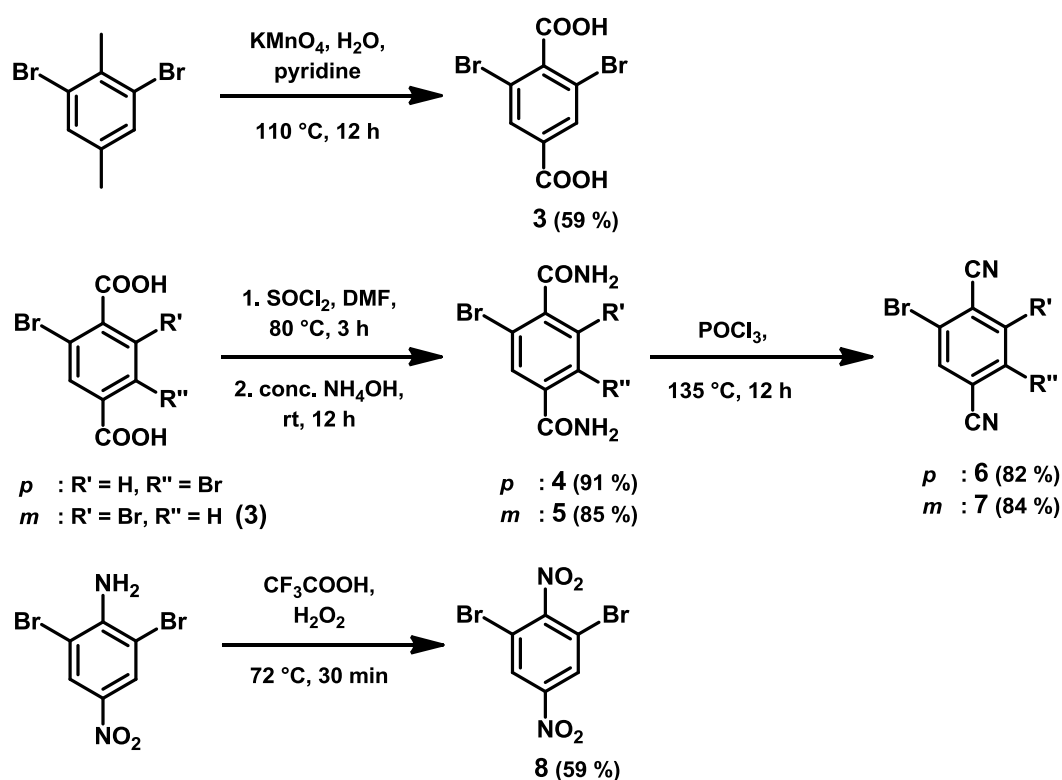
## Synthesis of the bridging units

1,4-Diiodo-2,5-dimethoxybenzene,<sup>14</sup> 2,5-dibromo-*para*-xylene,<sup>15</sup> 1,4-dibromo-2,5-dinitrobenzene,<sup>16</sup> 2,6-dibromo-*para*-xylene,<sup>17</sup> 1,3-dibromo-2,5-dichlorobenzene,<sup>18</sup> 2,4-dibromo-3,6-dimethoxyaniline,<sup>19</sup> 2,5-dibromoterephthalic acid,<sup>20</sup> 2,6-dibromo-4-

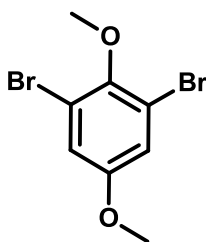
nitroaniline<sup>21</sup> and 1,3-diiodo-4,6-dimethoxybenzene<sup>22</sup> were synthesized following reported procedures.



**Scheme S1.** Synthesis of 1,3-diiodo-2,5-dimethoxybenzene.



**Scheme S2.** Synthesis of 2,5- and 2,6-dibromoterephthonitrile (**6**, **7**) and 1,3-dibromo-2,5-dinitrobenzene (**8**).

**1,3-Dibromo-2,5-methoxybenzene (1)**

**CA:** [74076-59-8].

Synthesis according to literature.<sup>15</sup>

A suspension of 2,4-dibromo-3,6-dimethoxyaniline (1.84 g, 5.92 mmol) in EtOH (14 ml) and benzene (2.5 ml) was heated and conc. H<sub>2</sub>SO<sub>4</sub> (4 ml) and then sodium nitrite (857 mg, 12.4 mmol) were added. When the foaming stopped, the reaction was heated under reflux for 3 h until the gas formation stopped. After cooling to rt the solution was acidified with aqueous HCl solution and extracted with DCM (3 x 30 ml). The combined organic phase was washed with H<sub>2</sub>O (2 x 30 ml) and dried over MgSO<sub>4</sub>. The crude product was purified by flash chromatography on silica gel (DCM:PE, 1:1).

**Yield:** 1.49 g (5.03 mmol, 85 %), colorless oil.

**Formula:** C<sub>8</sub>H<sub>8</sub>Br<sub>2</sub>O<sub>2</sub> [295.96].

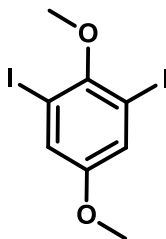
**<sup>1</sup>H-NMR (400.1 MHz, CDCl<sub>3</sub>):**

δ [ppm] = 7.05 (s, 2 H), 3.83 (s, 3 H), 3.75 (s, 3 H).

**<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):**

δ [ppm] = 156.5 (C<sub>q</sub>), 148.2 (C<sub>q</sub>), 118.3 (CH), 60.9 (CH<sub>3</sub>), 56.1 (CH<sub>3</sub>), 53.6 (C<sub>q</sub>).

**EI-MS:** 295.9 m/z.

**1,3-Diiodo-2,5-dimethoxybenzene (2)**

**CA:** [744216-14-6].

Synthesis according to literature.<sup>23</sup>

Under a nitrogen atmosphere CuI (38.6 mg, 203  $\mu$ mol) and NaI (6.08 g, 40.6 mmol) were added to 1,4-dioxane (8 ml) and the mixture was degassed for 10 min. Trans-*N,N*-dimethyl-1,2-cyclohexandiamine (57.7 mg, 405  $\mu$ mol) and 1,3-dibromo-2,5-dimethoxybenzene (**1**, 300 mg, 1.01 mmol) were added and the mixture was heated at 110 °C for 3 d. After cooling to rt the solvent was removed *in vacuo*. Ammonium hydroxide (30 %, 20 ml) and water (40 ml) were added to the residue. The aqueous phase was extracted with DCM. The organic phase was dried with MgSO<sub>4</sub> and the solvent was removed *in vacuo*. The crude product was purified by chromatography on silica gel (PE:DCM, 1:1).

**Yield:** 294 mg (754  $\mu$ mol, 73 %), colorless solid.

**Formula:** C<sub>8</sub>H<sub>8</sub>I<sub>2</sub>O<sub>2</sub> [389.96].

**<sup>1</sup>H-NMR (400.1 MHz, CDCl<sub>3</sub>):**

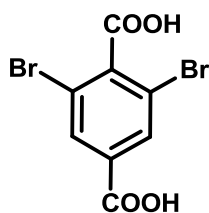
$\delta$  [ppm] = 7.30 (s, 2 H), 3.80 (s, 3 H), 3.73 (s, 3 H).

**<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):**

$\delta$  [ppm] = 156.9 (C<sub>q</sub>), 153.1 (C<sub>q</sub>), 125.2 (CH), 89.8 (C<sub>q</sub>), 61.0 (CH<sub>3</sub>), 56.1 (CH<sub>3</sub>).

**EI-MS:** 389.7 m/z



**2,6-Dibromoterephthalic acid (3)****CA:** [22191-58-8].Synthesis according to literature.<sup>20</sup>

2,6-Dibromo-*p*-xylene (2.64 g, 10.0 mmol) and  $\text{KMnO}_4$  (7.90 g, 50.0 mmol) were added to a mixture of pyridine (20 ml) and water (10 ml) and the mixture was heated to reflux. Then  $\text{KMnO}_4$  (3.00 g, 19.0 mmol) dissolved in water (10 ml) was added in 4 steps in 30 min intervals. After refluxing overnight, the mixture was filtered through celite. The mixture was concentrated by vacuum distillation and an aqueous HCl solution (10 %, 10 ml) was added to the filtrate. The resulting precipitate was extracted by EA (3 x 10 ml), dried over  $\text{MgSO}_4$ , filtered and the solvent was evaporated *in vacuo*.

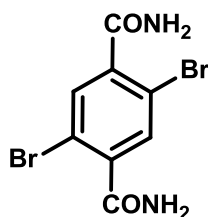
**Yield:** 1.90 g (5.86 mmol, 59 %), colorless solid.**Formular:**  $\text{C}_8\text{H}_4\text{Br}_2\text{O}_4$  [323.92]. **$^1\text{H-NMR}$  (400.1 MHz,  $(\text{CD}_3)_2\text{SO}$ ):**

$\delta$  [ppm] = 8.10 (s, 2 H). *The signal of the protons of the carboxyl group is missing. This is probably due to exchange of the protons with the deuterated solvent.*

 **$^{13}\text{C-NMR}$  (100.6 MHz,  $(\text{CD}_3)_2\text{SO}$ ):**

$\delta$  [ppm] = 166.6 ( $\text{C}_q$ ), 164.5 ( $\text{C}_q$ ), 142.2 ( $\text{C}_q$ ), 134.0 ( $\text{C}_q$ ), 132.1 (CH), 118.7 ( $\text{C}_q$ ).

**EI-MS:** 323.9 m/z

**2,5-Dibromoterephthalamide (4)**

**CA:** [50880-39-2].

Synthesis according to literature.<sup>24</sup>

The mixture of 2,5-dibromoterephthalic acid (4.00 g, 12.3 mmol), thionyl chloride (55 ml) and five drops of DMF was refluxed for 3 h. The solvent was removed *in vacuo*, and the crude product was dissolved in 1,4-dioxane (60 ml). Ammonium hydroxide (50 ml, conc.) was added dropwise to the mixture and stirred overnight at room temperature. The precipitate was filtered off and washed with 1,4-dioxane.

**Yield:** 3.60 g (11.2 mmol, 91 %), colorless solid.

**Formular:** C<sub>8</sub>H<sub>6</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub> [321.95].

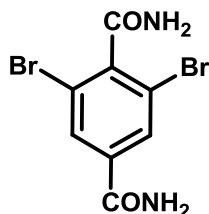
**<sup>1</sup>H-NMR (400.1 MHz, (CD<sub>3</sub>)SO):**

δ [ppm] = 7.98 (s, 2 H), 7.67 (s, 2 H), 7.63 (s, 2 H). *The four protons of the carboxamides give two signals.*

**<sup>13</sup>C-NMR (100.6 MHz, (CD<sub>3</sub>)SO):**

δ [ppm] = 167.2 (C<sub>q</sub>), 140.9 (C<sub>q</sub>), 132.3 (CH), 117.7 (C<sub>q</sub>).

**EI-MS:** 321.9 m/z

**2,6-Dibromoterephthalamide (5)**

Synthesis according to literature.<sup>24</sup>

The mixture of 2,6-dibromoterephthalic acid (**3**, 750 mg, 2.32 mmol), thionyl chloride (14 ml) and a drop of DMF was refluxed for 3 h. The solvent was removed *in vacuo*, and the crude product was dissolved in 1,4-dioxane (15 ml). Ammonium hydroxide (15 ml, conc.) was added dropwise to the mixture and stirred overnight at rt. The precipitate was filtered off and washed with 1,4-dioxane.

**Yield:** 613 mg (1.96 mmol, 85 %), colorless solid.

**Formular:** C<sub>8</sub>H<sub>6</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub> [321.95].

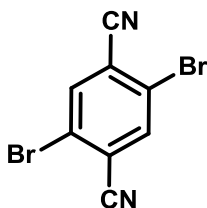
**<sup>1</sup>H-NMR (400.1 MHz(CD<sub>3</sub>)<sub>2</sub>SO):**

δ [ppm] = 8.19 (s, 1 H), 8.09 (s, 2 H), 8.08 (s, 1H), 7.81 (s, 1 H), 7.65 (s, 1 H).

**<sup>13</sup>C-NMR (100.6 MHz, (CD<sub>3</sub>)<sub>2</sub>SO):**

δ [ppm] = 167.0 (C<sub>q</sub>), 164.6 (C<sub>q</sub>), 142.9 (C<sub>q</sub>), 136.5 (C<sub>q</sub>), 130.6 (CH), 119.5 (C<sub>q</sub>).

**EI-MS:** 321.8 m/z

**2,5-Dibromoterephthalonitrile (6)**

**CA:** [18870-11-6].

Synthesis according to literature.<sup>24-25</sup>

2,5-Dibromoterephthalamide (**4**, 250 mg, 777  $\mu$ mol) was dissolved in phosphorus oxychloride (12 ml) and heated at 125 °C for 12 h. The cooled mixture was slowly poured into ice water (50 ml) and stirred for 15 min. The resulting precipitate was filtered off, washed with water and dried *in vacuo*.

**Yield:** 182 mg (637  $\mu$ mol, 82 %), colorless solid.

**Formular:** C<sub>8</sub>H<sub>2</sub>Br<sub>2</sub>N<sub>2</sub> [285.92].

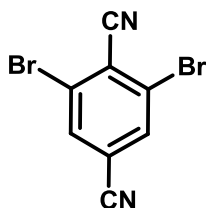
**<sup>1</sup>H-NMR (400.1 MHz, CDCl<sub>3</sub>):**

$\delta$  [ppm] = 7.96 (s, 2 H).

**<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):**

$\delta$  [ppm] = 138.0 (C<sub>q</sub>), 124.4 (C<sub>q</sub>), 121.3 (CH), 114.7 (C<sub>q</sub>).

**EI-MS:** 285.9 m/z

**2,6-Dibromoterephthalonitrile (7)**

Synthesis according to literature.<sup>24-25</sup>

2,6-Dibromoterephthalamide (**5**, 300 mg, 932  $\mu\text{mol}$ ) was dissolved in phosphorus oxychloride (12 ml) and heated at 125 °C for 12 h. The cooled mixture was slowly poured into ice water (50 ml) and stirred for 15 min. The resulting precipitate was filtered, washed with water and dried *in vacuo*.

**Yield:** 223 mg (780  $\mu\text{mol}$ , 84 %), colorless solid.

**Formular:**  $\text{C}_8\text{H}_2\text{Br}_2\text{N}_2$  [285.92].

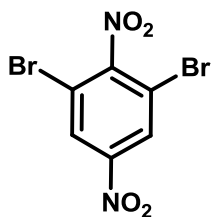
**$^1\text{H}$ -NMR (400.1 MHz,  $\text{CDCl}_3$ ):**

$\delta$  [ppm] = 7.93 (s, 2 H).

**$^{13}\text{C}$ -NMR (100.6 MHz,  $\text{CDCl}_3$ ):**

$\delta$  [ppm] = 134.7 (CH), 127.7 ( $\text{C}_q$ ), 123.3 ( $\text{C}_q$ ), 118.2 ( $\text{C}_q$ ), 114.84 ( $\text{C}_q$ ), 114.76 ( $\text{C}_q$ ).

**EI-MS:** 285.8 m/z

**1,3-Dibromo-2,5-dinitrobenzene (8)**

Synthesis according to literature.<sup>26</sup>

A solution of 2,6-dibromo-4-nitroaniline (500 mg, 1.69 mmol) in (20 ml) trifluoroacetic acid (20 ml) was heated under reflux. H<sub>2</sub>O<sub>2</sub> (6 ml, 30 %) was added over a period of 15 min. The mixture was heated under reflux for additional 15 min, cooled to rt and poured on crushed ice and water (20 ml). The resulting precipitate was collected by filtration.

**Yield:** 467 mg (1.43 mmol, 85 %), colorless solid.

**Formula:** C<sub>6</sub>H<sub>2</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>4</sub> [325.90].

**<sup>1</sup>H-NMR (400.1 MHz, CDCl<sub>3</sub>):**

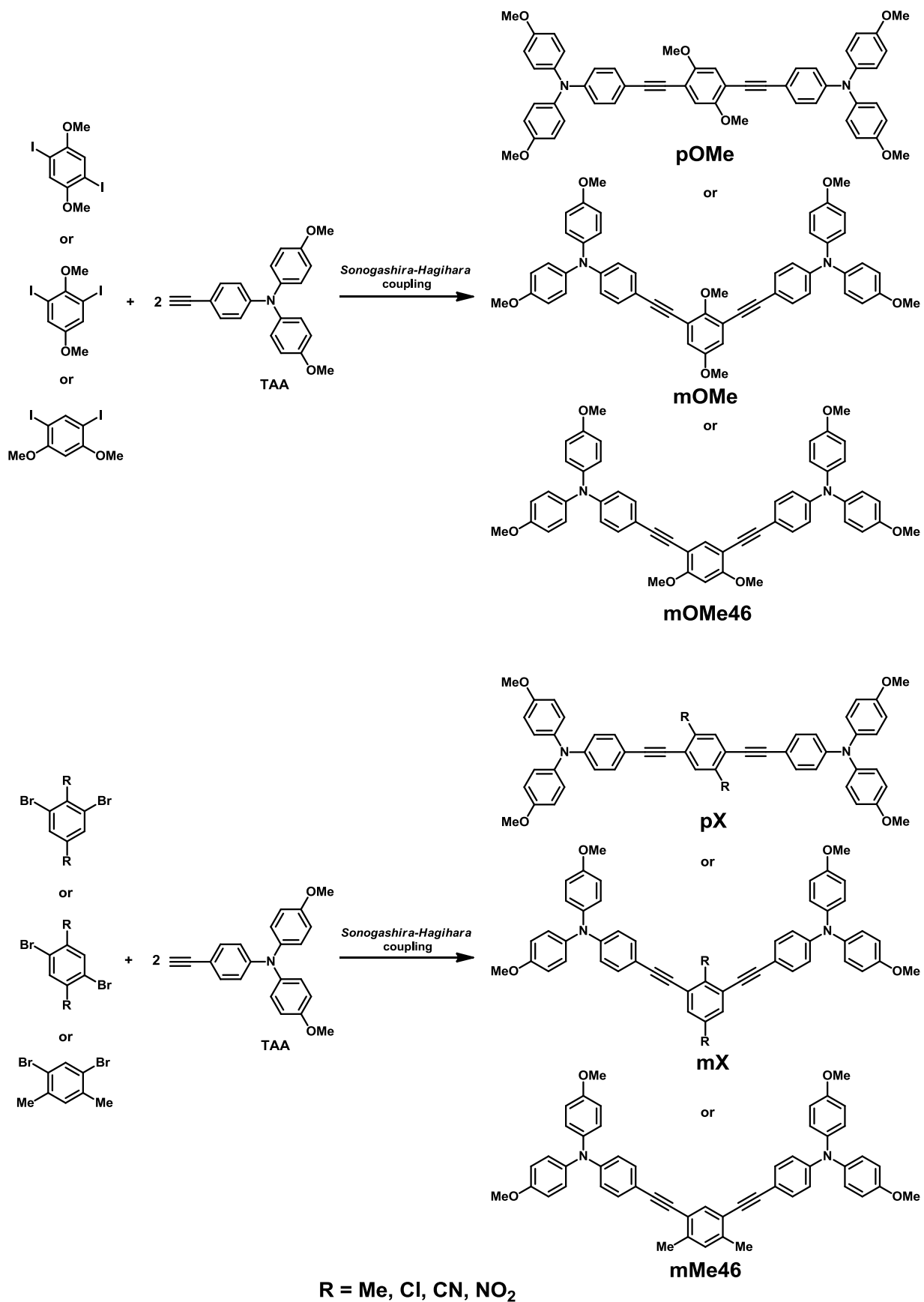
δ [ppm] = 8.51 (s, 2 H).

**<sup>13</sup>C-NMR (100.6 MHz, CDCl<sub>3</sub>):**

δ [ppm] = 154.9 (C<sub>q</sub>), 147.9 (C<sub>q</sub>), 128.2 (CH), 115.1 (C<sub>q</sub>).

**EI-MS:** 325.8 m/z

# Synthesis of the bistriarylamines

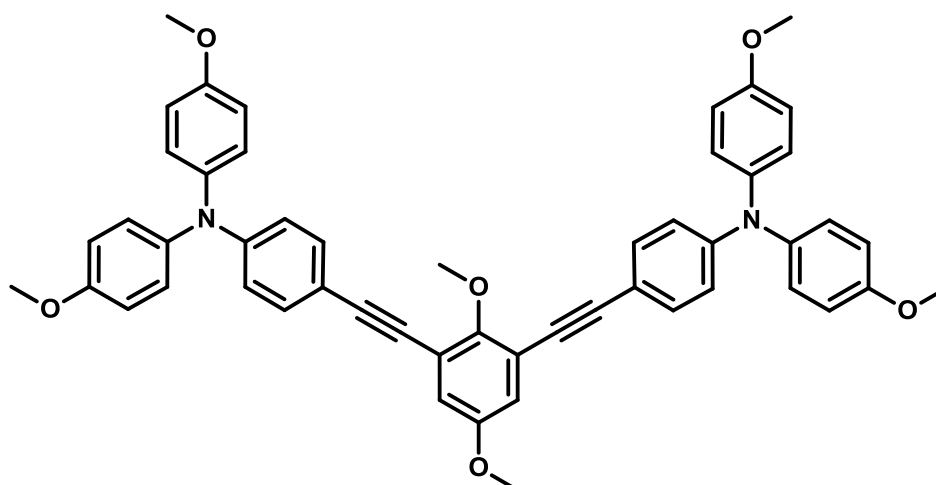


**Scheme S3.** Synthesis of the bistriarylamines *via* Sonogashira-Hagihara coupling.

The triarylamine *N,N*-bis(4-methoxyphenyl)-*N*-(4-(ethynyl)phenyl)amine (**TAA**),<sup>27</sup> 1,4-bis{4-[*N,N*-di(4-methoxyphenyl)amino]phenylethynyl}(2,5-dimethoxy)benzene (**pOMe**)<sup>28</sup> and 1,4-bis{4-[*N,N*-di(4-methoxyphenyl)amino]phenylethynyl}(2,5-dimethyl)benzene (**pMe**)<sup>29</sup> were synthesized following reported procedures.

The following *Sonogashira-Hagihara* coupling reactions were performed according to literature.<sup>28-30</sup>

**mOMe**      **1,3-Bis{4-[*N,N*-di(4-methoxyphenyl)amino]phenylethynyl}(2,5-dimethoxy)benzene**



Under a nitrogen atmosphere 1,3-diiodo-2,5-dimethoxybenzene (**2**, 110 mg, 282  $\mu\text{mol}$ ),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (7.92 mg, 11.3  $\mu\text{mol}$ ) and  $\text{CuI}$  (1.07 mg, 5.64  $\mu\text{mol}$ ) were dissolved in  $\text{NEt}_3$  (4 ml). **TAA** (204 mg, 619  $\mu\text{mol}$ ) in THF (4 ml) was added to the solution and the mixture was degassed. The reaction mixture was stirred in the dark for 3 d. The solvent was removed *in vacuo*. The residue was dissolved in DCM and was washed with water. The organic phase was dried with  $\text{MgSO}_4$  and the solvent removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (DCM).

**Yield:** 200 mg (252  $\mu\text{mol}$ , 89 %), yellow solid.

**Formula:**  $\text{C}_{52}\text{H}_{44}\text{N}_2\text{O}_6$  [792.92].



**<sup>1</sup>H-NMR (600.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):**

$\delta$  [ppm] = 7.32 (AA', 4 H), 7.08 (AA', 8 H), 6.94 (s, 2 H), 6.87 (BB', 8 H), 6.82 (BB', 4 H), 4.00 (s, 3 H), 3.79 (s, 12 H), 3.78 (s, 3 H).

**<sup>13</sup>C-NMR (150.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>):**

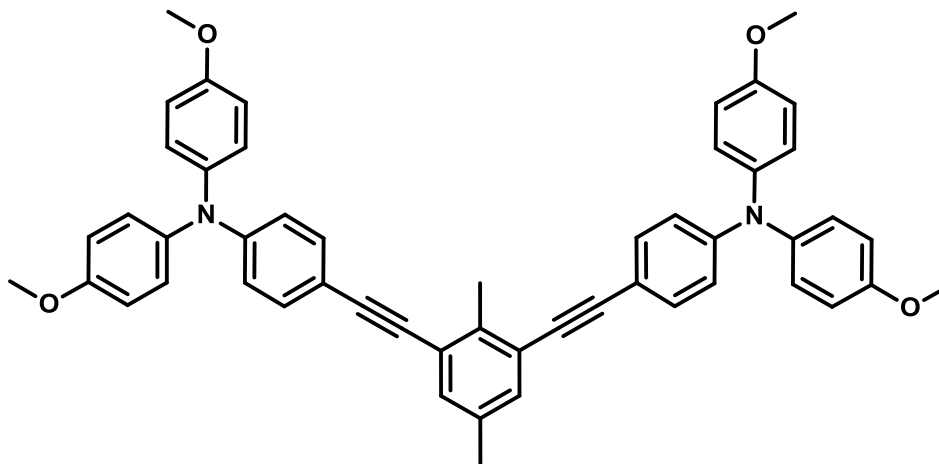
$\delta$  [ppm] = 157.0 (C<sub>q</sub>), 155.8 (C<sub>q</sub>), 155.4 (C<sub>q</sub>), 149.6 (C<sub>q</sub>), 140.3 (C<sub>q</sub>), 132.7 (CH), 127.7 (CH), 119.01 (C<sub>q</sub>), 119.00 (CH), 118.0 (CH), 115.2 (CH), 113.6 (C<sub>q</sub>), 94.6 (C<sub>q</sub>), 84.2 (C<sub>q</sub>), 61.6 (CH<sub>3</sub>), 56.1 (CH<sub>3</sub>), 55.8 (CH<sub>3</sub>).

**ESI-MS (M<sup>+</sup>, high resolution):**

calc.: 792.31939 m/z

exp.: 792.31953 m/z       $\Delta$  = 0.18 ppm

**mMe**      **1,3-Bis{4-[*N,N*-di(4-methoxyphenyl)amino]phenylethynyl}(2,5-dimethyl)benzene**



Under a nitrogen atmosphere 2,6-dibromo-*para*-xylene (55.0 mg, 208  $\mu\text{mol}$ ), **TAA** (151 mg, 458  $\mu\text{mol}$ ),  $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$  (17.6 mg, 25.1  $\mu\text{mol}$ ),  $\text{CuI}$  (3.17 mg, 16.6  $\mu\text{mol}$ ),  $\text{P}^t\text{Bu}_3$  (167  $\mu\text{l}$  of a 1.00 M solution in *n*-hexane, 167  $\mu\text{mol}$ ) and  $\text{HN}^i\text{Pr}_2$  (76.0 mg, 751  $\mu\text{mol}$ ) were dissolved in 1,4-dioxane (4 ml) and degassed. The reaction mixture was stirred in the dark for 3 d. The solvent was removed *in vacuo*, the residue was dissolved in DCM and washed with water. The organic phase was dried with  $\text{MgSO}_4$  and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (DCM:PE, 3:1).

**Yield:** 103 mg (135  $\mu\text{mol}$ , 66 %), pale green solid.

**Formula:**  $\text{C}_{52}\text{H}_{44}\text{N}_2\text{O}_4$  [760.92].

**$^1\text{H}$ -NMR (600.1 MHz,  $\text{CD}_2\text{Cl}_2$ ):**

$\delta$  [ppm] = 7.31 (AA', 4 H), 7.24 (dd,  $^4J_{\text{HH}} = 0.6$  Hz,  $^5J_{\text{HH}} = 0.4$  Hz, 2 H), 7.08 (AA', 8 H), 6.86 (BB', 8 H), 6.82 (BB', 4 H), 3.79 (s, 12 H), 2.61 (d,  $^5J_{\text{HH}} = 0.4$  Hz, 3 H), 2.29 (d,  $^4J_{\text{HH}} = 0.6$  Hz, 3 H).

**$^{13}\text{C}$ -NMR (150.9 MHz,  $\text{CD}_2\text{Cl}_2$ ):**

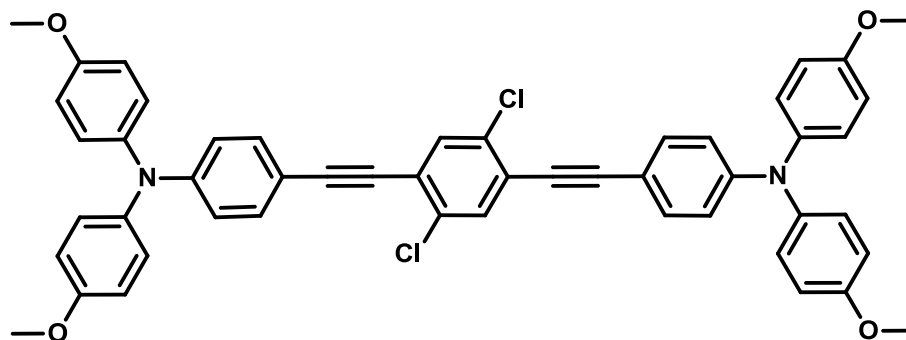
$\delta$  [ppm] = 156.9 (C<sub>q</sub>), 149.4 (C<sub>q</sub>), 140.4 (C<sub>q</sub>), 138.7 (C<sub>q</sub>), 135.5 (C<sub>q</sub>), 132.6 (CH), 132.2 (CH), 127.6 (CH), 124.1 (C<sub>q</sub>), 119.2 (CH), 115.1 (CH), 114.1 (C<sub>q</sub>), 94.1 (C<sub>q</sub>), 87.2 (C<sub>q</sub>), 55.8 (CH<sub>3</sub>), 20.7 (CH<sub>3</sub>), 18.9 (CH<sub>3</sub>).

**ESI-MS (M<sup>+</sup>, high resolution):**

calc.: 760.32956 m/z

exp.: 760.32931 m/z  $\Delta$  = 0.33 ppm

**pCl**      **1,4-Bis{4-[N,N-di(4-methoxyphenyl)amino]phenylethynyl}(2,5-dichloro)benzene**



Under a nitrogen atmosphere 1,4-dibromo-2,5-dichlorobenzene (60.0 mg, 197  $\mu$ mol), **TAA** (130 mg, 395  $\mu$ mol), Pd(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub>Cl<sub>2</sub> (9.82 mg, 26.0  $\mu$ mol), CuI (3.64 mg, 19.1  $\mu$ mol), P<sup>t</sup>Bu<sub>3</sub> (57.0  $\mu$ l of a 1.00 M solution in *n*-hexane, 57.0  $\mu$ mol) and HN<sup>i</sup>Pr<sub>2</sub> (88.0 mg, 866  $\mu$ mol) were dissolved in 1,4-dioxane (8 ml) and degassed. The reaction mixture was stirred for 3 d in the dark. The solvent was removed *in vacuo*, the residue was dissolved in DCM and washed with water. The organic phase was dried with MgSO<sub>4</sub> and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (PE:DCM, 1:1).

**Yield:** 50.0 mg (62.4  $\mu$ mol, 32 %), yellow solid.

**Formula:** C<sub>50</sub>H<sub>38</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub> [801.75].

**<sup>1</sup>H-NMR (600.1 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):**

$\delta$  [ppm] = 7.69 (s, 2 H), 7.38 (AA', 4 H), 7.14 (AA', 8 H), 6.96 (BB', 8 H), 6.79 (BB', 4 H), 3.81 (s, 12 H).

<sup>13</sup>C-NMR (150.9 MHz, (CD<sub>3</sub>)<sub>2</sub>CO):

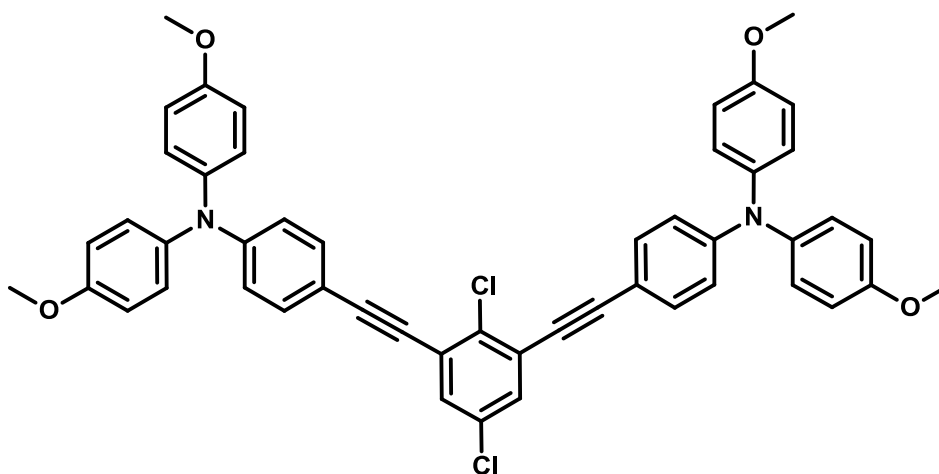
$\delta$  [ppm] = 158.0 (C<sub>q</sub>), 150.1 (C<sub>q</sub>), 140.4 (C<sub>q</sub>), 134.0 (C<sub>q</sub>), 133.6 (CH), 133.4 (CH), 128.7 (CH), 124.9 (C<sub>q</sub>), 118.6 (CH), 115.9 (CH), 112.7 (C<sub>q</sub>), 99.4 (C<sub>q</sub>), 84.6 (C<sub>q</sub>), 55.8 (CH<sub>3</sub>).

ESI-MS (M<sup>+</sup>, high resolution):

calc.: 800.22032 m/z

exp.: 800.22052 m/z  $\Delta$  = 0.25 ppm

mCl 1,3-Bis{4-[N,N-di(4-methoxyphenyl)amino]phenylethynyl}(2,5-dichloro)benzene



Under a nitrogen atmosphere 1,3-dibromo-2,5-dichlorobenzene (70.0 mg, 230  $\mu$ mol), **TAA** (152 mg, 461  $\mu$ mol), Pd(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub>Cl<sub>2</sub> (11.5 mg, 30.0  $\mu$ mol), CuI (4.24 mg, 22.2  $\mu$ mol), P<sup>t</sup>Bu<sub>3</sub> (67.0  $\mu$ l of a 1.00 M solution in *n*-hexane, 67.0  $\mu$ mol) and HN<sup>i</sup>Pr<sub>2</sub> (102 mg, 1.01 mmol) were dissolved in 1,4-dioxane (9 ml) and degassed. The reaction mixture was stirred in the dark for 3 d. The solvent was removed *in vacuo*, the residue was dissolved in DCM and washed with water. The organic phase was dried with MgSO<sub>4</sub> and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (PE:DCM, 1:2).

**Yield:** 64.0 mg (79.8  $\mu$ mol, 35 %), yellow solid.

**Formula:**  $C_{50}H_{38}Cl_2N_2O_4$  [801.75].

**$^1H$ -NMR (600.1 MHz,  $(CD_3)_2CO$ ):**

$\delta$  [ppm] = 7.54 (s, 2 H), 7.38 (AA', 4 H), 7.13 (AA', 8 H), 6.95 (BB', 8 H), 6.79 (BB', 4 H), 3.81 (s, 12 H).

**$^{13}C$ -NMR (150.9 MHz,  $(CD_3)_2CO$ ):**

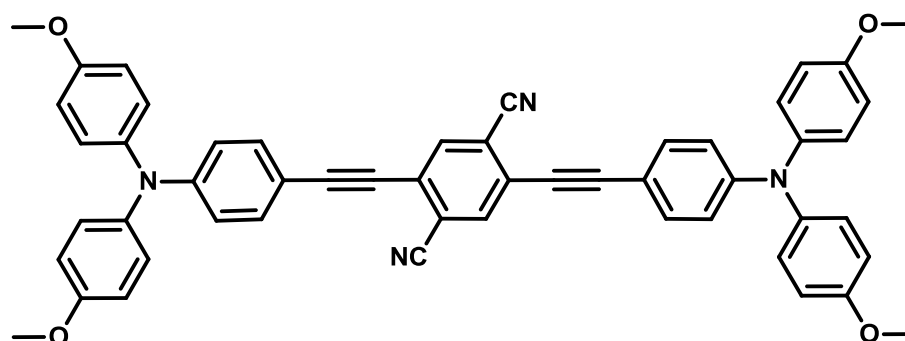
$\delta$  [ppm] = 158.0 ( $C_q$ ), 150.9 ( $C_q$ ), 140.4 ( $C_q$ ), 135.2 ( $C_q$ ), 133.6 (CH), 132.7 ( $C_q$ ), 131.9 (CH), 128.6 (CH), 126.7 ( $C_q$ ), 118.7 (CH), 115.8 (CH), 112.6 ( $C_q$ ), 98.3 ( $C_q$ ), 84.4 ( $C_q$ ), 55.8 ( $CH_3$ ).

**ESI-MS ( $M^{+}$ , high resolution):**

calc.: 800.22032 m/z

exp.: 800.22070 m/z  $\Delta$  = 0.47 ppm

**pCN**      **1,4-Bis{4-[*N,N*-di(4-methoxyphenyl)amino]phenylethynyl}(2,5-dicyano)benzene**



Under a nitrogen atmosphere **TAA** (127 mg, 385  $\mu$ mol),  $Pd(PPh_3)_2Cl_2$  (11.3 mg, 16.1  $\mu$ mol) and  $CuI$  (1.54 mg, 8.08  $\mu$ mol) were dissolved in  $NEt_3$  (7 ml). 2,5-Dibromoterephthalonitrile (**7**, 55.0 mg, 192  $\mu$ mol) in THF (2 ml) was added to the solution and the mixture was degassed. The reaction mixture was stirred in the dark for 3 d. The solvent was removed *in vacuo*, the residue was dissolved in DCM and washed with water.

The organic phase was dried with  $\text{MgSO}_4$  and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (PE:DCM, 1:2).

**Yield:** 134 mg (171  $\mu\text{mol}$ , 89 %), red solid.

**Formula:**  $\text{C}_{52}\text{H}_{38}\text{N}_4\text{O}_4$  [782.88].

**$^1\text{H-NMR}$  (600.1 MHz,  $(\text{CD}_3)_2\text{CO}$ ):**

$\delta$  [ppm] = 8.12 (s, 2 H), 7.42 (AA', 4 H), 7.17 (AA', 8 H), 6.97 (BB', 8 H), 6.80 (BB', 4 H), 3.81 (s, 12 H).

**$^{13}\text{C-NMR}$  (150.9 MHz,  $(\text{CD}_3)_2\text{CO}$ ):**

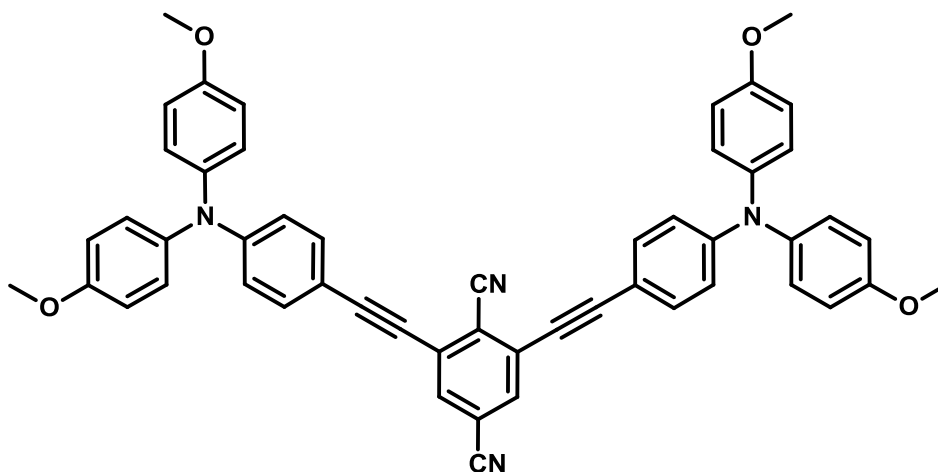
$\delta$  [ppm] = 158.2 ( $\text{C}_q$ ), 151.5 ( $\text{C}_q$ ), 140.1 ( $\text{C}_q$ ), 136.5 (CH), 133.9 (CH), 128.8 (CH), 127.0 ( $\text{C}_q$ ), 118.9 ( $\text{C}_q$ ), 118.3 (CH), 116.7 ( $\text{C}_q$ ), 115.9 (CH), 111.4 ( $\text{C}_q$ ), 101.6 ( $\text{C}_q$ ), 84.6 ( $\text{C}_q$ ), 55.8 ( $\text{CH}_3$ ).

**ESI-MS ( $\text{M}^{++}$ , high resolution):**

calc.: 782.28876 m/z

exp.: 782.28841 m/z  $\Delta = 0.45$  ppm

**mCN** 1,3-Bis{4-[*N,N*-di(4-methoxyphenyl)amino]phenylethynyl}(2,5-dicyano)benzene



Under a nitrogen atmosphere **TAA** (177 mg, 537  $\mu\text{mol}$ ),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (14.4 mg, 20.5  $\mu\text{mol}$ ) and  $\text{CuI}$  (1.96 mg, 10.3  $\mu\text{mol}$ ) were dissolved in  $\text{NEt}_3$  (10 ml). 2,6-Dibromotetraphthalonitrile (**6**, 70.0 mg, 245  $\mu\text{mol}$ ) in THF (3 ml) was added to the solution and the mixture was degassed. The reaction mixture was stirred in the dark for 3 d. The solvent was removed *in vacuo*, the residue was dissolved in DCM and washed with water. The organic phase was dried with  $\text{MgSO}_4$  and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (PE:DCM, 1:2).

**Yield:** 180 mg (230  $\mu\text{mol}$ , 94 %), red solid.

**Formula:**  $\text{C}_{52}\text{H}_{38}\text{N}_4\text{O}_4$  [782.88].

**$^1\text{H}$ -NMR (600.1 MHz,  $(\text{CD}_3)_2\text{CO}$ ):**

$\delta$  [ppm] = 7.99 (s, 2 H), 7.43 (AA', 4 H), 7.17 (AA', 8 H), 6.97 (BB', 8 H), 6.80 (BB', 4 H), 3.81 (s, 12 H).

**$^{13}\text{C}$ -NMR (150.9 MHz,  $(\text{CD}_3)_2\text{CO}$ ):**

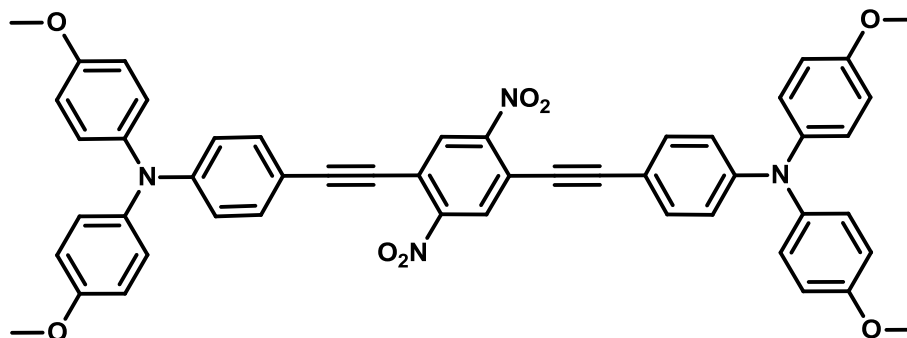
$\delta$  [ppm] = 158.2 ( $\text{C}_q$ ), 151.6 ( $\text{C}_q$ ), 140.1 ( $\text{C}_q$ ), 134.0 (CH), 133.8 (CH), 130.1 ( $\text{C}_q$ ), 128.8 (CH), 120.1 ( $\text{C}_q$ ), 118.3 (CH), 117.5 ( $\text{C}_q$ ), 117.1 ( $\text{C}_q$ ), 116.3 ( $\text{C}_q$ ), 115.9 (CH), 111.3 ( $\text{C}_q$ ), 100.5 ( $\text{C}_q$ ), 84.2 ( $\text{C}_q$ ), 55.8 ( $\text{CH}_3$ ).

**ESI-MS ( $\text{M}^+$ , high resolution):**

calc.: 782.28876 m/z

exp.: 782.28926 m/z  $\Delta = 0.64$  ppm

**pNO<sub>2</sub>**      **1,4-Bis{4-[*N,N*-di(4-methoxyphenyl)amino]phenylethynyl}(2,5-dinitro)benzene**



Under a nitrogen atmosphere 1,4-dibromo-2,5-dinitrobenzene (70.0 mg, 215  $\mu$ mol), **TAA** (156 mg, 474  $\mu$ mol Pd(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub>Cl<sub>2</sub> (9.91 mg, 26.8  $\mu$ mol), CuI (9.00 mg, 47.3  $\mu$ mol) and NEt<sub>3</sub> (2 ml) were dissolved in toluene (8 ml) and degassed. The reaction mixture was stirred in the dark for 3 d. The solvent was removed *in vacuo*, the residue was dissolved in DCM and washed with water. The organic phase was dried with MgSO<sub>4</sub> and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (PE:DCM, 1:2).

**Yield:**                      85.0 mg (103  $\mu$ mol, 48 %), red solid.

**Formula:**                C<sub>50</sub>H<sub>38</sub>N<sub>4</sub>O<sub>8</sub> [822.86].

**<sup>1</sup>H-NMR (600.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):**

$\delta$  [ppm] =                8.28 (s, 2 H), 7.36 (AA', 4 H), 7.11 (AA', 8 H), 6.88 (BB', 8 H), 6.81 (BB', 4 H), 3.80 (s, 12 H).

**<sup>13</sup>C-NMR (150.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>):**

$\delta$  [ppm] =                157.4 (C<sub>q</sub>), 150.9 (C<sub>q</sub>), 150.5 (C<sub>q</sub>), 139.7 (C<sub>q</sub>), 133.7 (CH), 130.6 (CH), 128.1 (CH), 118.5 (C<sub>q</sub>), 118.2 (CH), 115.3 (CH), 111.3 (C<sub>q</sub>), 103.3 (C<sub>q</sub>), 83.6 (C<sub>q</sub>), 55.8 (CH<sub>3</sub>).

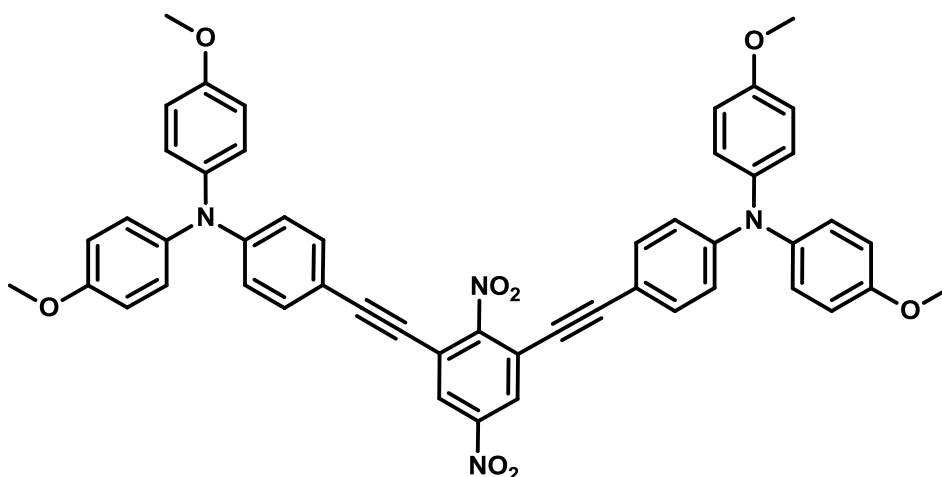
**ESI-MS (M<sup>+</sup>, high resolution):**



calc.: 822.26842 m/z

exp.: 822.26806 m/z  $\Delta = 0.44$  ppm.

**mNO<sub>2</sub>**      **1,3-Bis{4-[N,N-di(4-methoxyphenyl)amino]phenylethynyl}(2,5-dinitro)benzene**



Under a nitrogen atmosphere 1,3-dibromo-2,5-dinitrobenzene (**8**, 100 mg, 307  $\mu$ mol), TAA (222 mg, 675  $\mu$ mol), CuI (9.00 mg, 47.0  $\mu$ mol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (9.91 mg, 14.0  $\mu$ mol) and NEt<sub>3</sub> (2 ml) were dissolved in toluene (8 ml) and degassed. The reaction mixture was stirred in the dark for 3 d. The solvent was removed *in vacuo*, the residue was dissolved in DCM and washed with water. The organic phase was dried with MgSO<sub>4</sub> and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (PE:DCM, 1:2).

**Yield:** 108 mg (131  $\mu$ mol, 43 %), red solid.

**Formula:** C<sub>50</sub>H<sub>38</sub>N<sub>4</sub>O<sub>8</sub> [822.86].

**<sup>1</sup>H-NMR (600.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):**

$\delta$  [ppm] = 8.27 (s, 2 H), 7.30 (AA', 4 H), 7.10 (AA', 8 H), 6.87 (BB', 8 H), 6.79 (BB', 4 H), 3.79 (s, 12 H)

**<sup>13</sup>C-NMR (150.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>):**

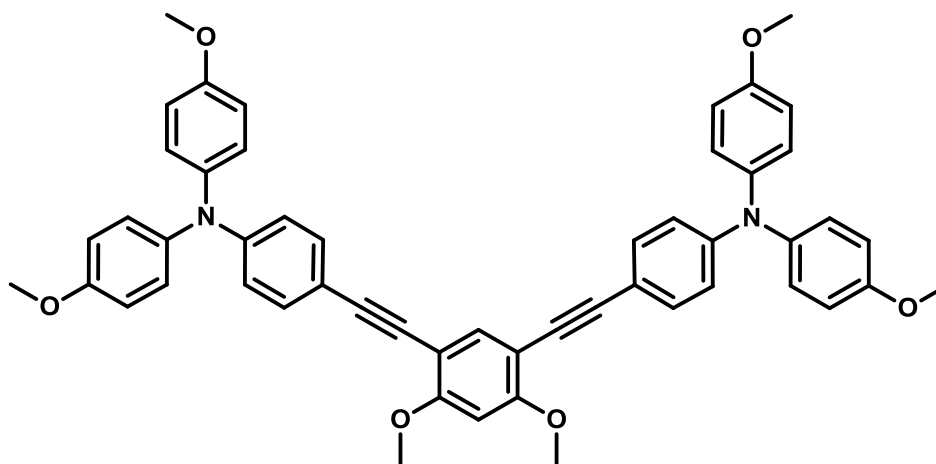
$\delta$  [ppm] = 157.4 (C<sub>q</sub>), 155.4 (C<sub>q</sub>), 150.9 (C<sub>q</sub>), 148.2 (C<sub>q</sub>), 139.7 (C<sub>q</sub>), 133.5 (CH), 128.1 (CH), 126.0 (CH), 119.8 (C<sub>q</sub>), 118.2 (CH), 115.3 (CH), 110.6 (C<sub>q</sub>), 100.9 (C<sub>q</sub>), 80.3 (C<sub>q</sub>), 55.8 (CH<sub>3</sub>).

**ESI-MS (M<sup>+</sup>, high resolution):**

calc.: 822.26842 m/z

exp.: 822.26836 m/z  $\Delta$  = 0.07 ppm

**mOMe46 1,3-Bis{4-[N,N-di(4-methoxyphenyl)amino]phenylethynyl}(4,6-dimethoxy)benzene**



Under a nitrogen atmosphere 1,3-diiodo-4,6-dimethoxybenzene (134 mg, 344  $\mu$ mol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (9.65 mg, 13.7  $\mu$ mol) and CuI (1.31 mg, 6.87  $\mu$ mol) were dissolved in NEt<sub>3</sub> (5 ml). **TAA** (249 mg, 756  $\mu$ mol) in THF (6 ml) was added to the solution and the mixture was degassed. The reaction mixture was stirred in the dark for 3 d. The solvent was removed *in vacuo*. The residue was dissolved in DCM and was washed with water. The organic phase was dried with MgSO<sub>4</sub> and the solvent removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (PE:DCM, 1:4  $\rightarrow$  DCM).

**Yield:** 240 mg (303  $\mu$ mol, 88 %), green solid.

**Formula:** C<sub>52</sub>H<sub>44</sub>N<sub>2</sub>O<sub>6</sub> [792.92].

**<sup>1</sup>H-NMR (600.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):**

δ [ppm] = 7.42 (s, 1 H), 7.26 (AA', 4 H), 7.08 (AA', 8 H), 6.94 (BB', 8 H), 6.72 (s, 1 H), 6.68 (BB', 4 H), 3.91 (s, 6 H), 3.75 (s, 12 H).

**<sup>13</sup>C-NMR (150.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>):**

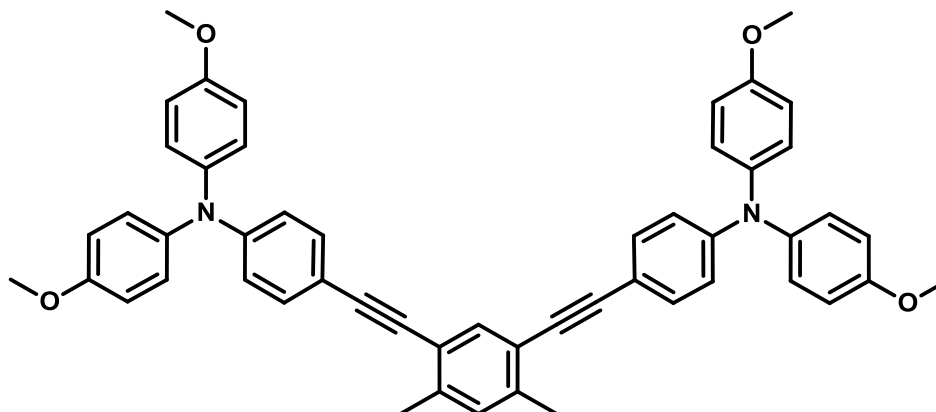
δ [ppm] = 160.8 (C<sub>q</sub>), 156.3 (C<sub>q</sub>), 148.5 (C<sub>q</sub>), 139.2 (C<sub>q</sub>), 136.2 (CH), 132.1 (CH), 127.5 (CH), 117.7 (CH), 115.1 (CH), 113.0 (C<sub>q</sub>), 104.2 (C<sub>q</sub>), 96.2 (CH), 92.5 (C<sub>q</sub>), 83.7 (C<sub>q</sub>), 56.61 (CH<sub>3</sub>), 56.3 (CH<sub>3</sub>).

**ESI-MS (M<sup>+</sup>, high resolution):**

calc.: 792.31939 m/z

exp.: 792.32006 m/z      Δ = 0.85 ppm

**mMe46      1,3-Bis{4-[*N,N*-di(4-methoxyphenyl)amino]phenylethynyl}(4,6-dimethyl)benzene**



Under a nitrogen atmosphere 4,6-dibromo-*meta*-xylene (60.0 mg, 227 μmol), **TAA** (165 mg, 500 μmol), Pd(C<sub>6</sub>H<sub>5</sub>CN)<sub>2</sub>Cl<sub>2</sub> (10.5 mg, 27.3 μmol), CuI (3.46 mg, 18.2 μmol), P<sup>t</sup>Bu<sub>3</sub> (182 μl of a 1.00 M solution in *n*-hexane, 182 μmol) and HN<sup>i</sup>Pr<sub>2</sub> (83.0 mg, 818 μmol) were dissolved in 1,4-dioxane (4.5 ml) and degassed. The reaction mixture was stirred in the dark for 3 d. The solvent was removed *in vacuo*, the residue was dissolved in DCM and washed with water. The organic phase was dried with MgSO<sub>4</sub> and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography on silica gel (PE: DCM, 1:3).

**Yield:** 79.0 mg (104  $\mu$ mol, 60 %), yellow solid.

**Formula:**  $C_{52}H_{44}N_2O_4$  [760.92].

**$^1H$ -NMR (600.1 MHz,  $CD_2Cl_2$ ):**

$\delta$  [ppm] = 7.53 (s, 1 H), 7.29 (AA', 4 H), 7.10 (s, 1 H), 7.07 (AA', 8 H), 6.86 (BB', 8 H), 6.83 (BB', 4 H), 3.79 (s, 12 H), 2.44 (s, 6 H).

**$^{13}C$ -NMR (150.9 MHz,  $CD_2Cl_2$ ):**

$\delta$  [ppm] = 156.9 ( $C_q$ ), 149.3 ( $C_q$ ), 140.4 ( $C_q$ ), 140.0 ( $C_q$ ), 134.5 (CH), 132.5 (CH), 131.1 (CH), 127.6 (CH), 121.4 (CH), 119.2 ( $C_q$ ), 115.1 ( $C_q$ ), 114.2 (CH), 94.0 ( $C_q$ ), 86.6 ( $C_q$ ), 55.8 ( $CH_3$ ), 20.8 ( $CH_3$ ).

**ESI-MS ( $M^{+}$ , high resolution):**

calc.: 760.3296 m/z

exp.: 760.3291 m/z  $\Delta$  = 0.66 ppm

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