

Supporting Information

Variation of Donor- and Acceptor Strength in Analogues of Brooker's Merocyanine and Generalization to Various Classes of Charge Transfer Compounds

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Determination of the 0-0 Band

We proceed in several steps:

- a) We perform a full nonlinear least-squares band fitting for the structured spectra, involving Gaussian shaped vibronic subbands.¹ From these fits, an average vibronic spacing Δv_{vib} is deduced.
- b) It is assumed that Δv_{vib} can be applied to all spectra including the unstructured ones.
- c) It is assumed that the band maxima correspond approximately to the energy of the 0-0 or of one of the higher vibronic bands.

The 0-0 energies are then given by eqs. S1 and S2, where n_{abs} and n_{fluo} are the number of vibronic quanta corresponding to the maximum of the absorption and fluorescence band.

$$v_{\text{max}}(\text{abs}) - n_{\text{abs}} * \Delta v_{\text{vib}} = v_{00}(\text{abs}) \quad (\text{S1})$$

$$v_{\text{max}}(\text{fluo}) + n_{\text{fluo}} * \Delta v_{\text{vib}} = v_{00}(\text{fluo}) \quad (\text{S2})$$

- d) The steepness of the red absorption and blue fluorescence tail is taken as an indicator for the number of vibronic quanta involved in the band maximum. A simple parameter, the wavenumber at a third of the maximum intensity, v_{3L} , can serve for this purpose as shown below. The correct performance of this simplified analysis is double-checked by comparing to the full band fitting analysis.

Several examples for this analysis are shown in Fig. S1. As can be seen from the third spectrum of Fig. S1, v_{3L} of the absorption spectrum corresponds fairly closely to v_{00} for $n_{\text{abs}} = 2$ (i.e. when the maximum corresponds to the 02 vibronic transition) or for larger n . We can

therefore use ν_{3L} for determining ν_{00} in the case of unstructured broad absorption bands using $\Delta\nu_{\text{vib}}$ and eq. S1. If the band maximum corresponds to the 00 or 01-transition (NO-DP in acetonitrile and diethyl ether, upper two spectra of Fig. S1), the difference between ν_{00} and ν_{3L} becomes larger but generally remains below ca 1000 cm^{-1} .

The analysis of all spectra in acetonitrile is contained in Table 1 of the main text, where ν_{00} is determined by varying $n_{\text{abs}} = 0, 1, 2$, etc. until the absolute value of $[\nu_{3L} - \nu_{00}(\text{abs})]$ is $< 1000\text{ cm}^{-1}$. In fact, for $n_{\text{abs}}=2$, this difference is only around 300 cm^{-1} and raises to ca 900 cm^{-1} in the case of $n_{\text{abs}}=0$ where the spectra are structured in all cases. These differences, especially for $n_{\text{abs}}=1$ and larger, are well below the vibrational spacing $\Delta\nu_{\text{vib}} = 1310\text{ cm}^{-1}$ determined by a fit of the upper 3 spectra in Fig. S1, and the assignment of n is therefore unambiguous.

e) A further parameter indicating directly the vibronic band at the maximum is the band halfwidth. It is around 2500 cm^{-1} for $n_{\text{abs}} = 0$, and ca 5000 cm^{-1} for $n_{\text{abs}}=2$, with values ranging in between for $n_{\text{abs}} = 1$. The difference between these values is consistent with multiples of $1200\text{-}1300\text{ cm}^{-1}$, i.e. close to the assumed vibronic spacing $\Delta\nu_{\text{vib}}$.

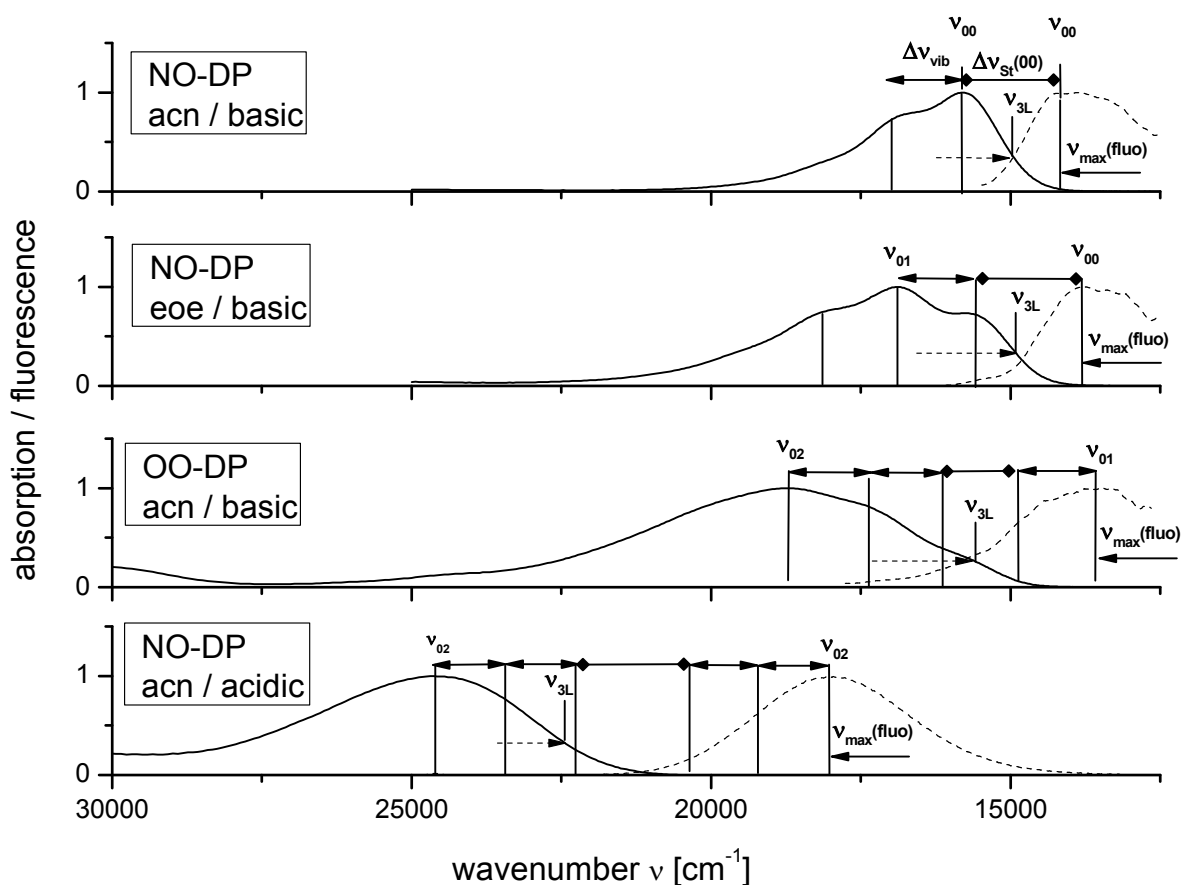


Figure S1: Schematic determination of $\nu_{00}(\text{abs})$ and $\nu_{00}(\text{fluo})$ from ν_{3L} , the intensity at a third of the maximum, for 4 different cases of structured and unstructured spectra. $\Delta\nu_{\text{St}}(00)$ is the Stokes shift as measured from the 00-energies. It is indicated graphically by filled diamonds. The vibrational spacing $\Delta\nu_{\text{vib}}$ is indicated by double arrows.

Table S1: Absorption and fluorescence characteristics of the basic forms of the dyes (a – NO-DP, b – NO-DT, c – OO-DP, d – SO-DP) as a function of polarity (EOE, EtOAc, THF, CH₂Cl₂, ACN) obtained from experimental spectra and by fitting (based on the solvatochromic spectral results and Gaussian fits for basic forms in respective Figs. 3a,b,c,d of the main text). Maximum $\nu_{\max}(\text{abs})$; halfwidth (FWHM) $\Delta\nu_{1/2}$; 00-band $\nu_{00}(\text{abs})$; vibrational quantum at the absorption maximum n_{abs} ; similar values for the fluorescence. Δf is the usual polarity function according to Lippert, rel I (01) is the relative intensity of vibrational subbands from band fitting.

Table S1a)

compound			EOE	EtOAc	THF	CH ₂ Cl ₂	ACN
NO-DP	absorption analysis	$\nu_{\max}(\text{abs})$	16900	16750	16650	15500	15800
		Δf	0.1669	0.19964	0.20957	0.21697	0.30542
		$\nu_{00}(\text{abs})$	15590	15440	15340	15500	15800
		$\Delta\nu_{1/2}$	3800	3500	3400	2900	2350
absorption fit	rel I (01) ^{a)}	1.40	1.17	1.11	0.87	0.67	
	n_{abs}	1	1	1	0	0	
	ν_{00}	15564	15477	15405	15439	15727	
fluorescence analysis	$\nu_{\max}(\text{fluo})$	13800				14200	
	$\nu_{00}(\text{fluo})$	13800	- ^{b)}	- ^{b)}	- ^{b)}	14200	
	n_{fluo}	0				0	

a) $\text{rel I (01)} = I(01) / I(00)$

b) not measured

Table S1b)

compound			EOE	EtOAc	THF	CH ₂ Cl ₂	ACN
NO-DT	absorption analysis	$\nu_{\max}(\text{exp})$	16750	16500	16350	16300	15350
		Δf	0.1669	0.19964	0.20957	0.21697	0.30542
		$\nu_{00}(\text{abs})$	15440	15190	15040	14990	15350
		$\Delta\nu_{1/2}$	4300	3950	3700	3600	2900
absorption fit	rel I (01) ^{a)}	1.60	1.37	1.18	1.11	0.86	
	n_{abs}	1	1	1	1	0	
	ν_{00}	15264	15121	15050	14995	15261	
fluorescence analysis	$\nu_{\max}(\text{fluo})$	13200	13100	13100	13100	13300	
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	$\nu_{00}(\text{fluo})$	13200	13100	13100	13100	13300	
	n_{fluo}	0	0	0	0	0	

a) $\text{rel I (01)} = I(01) / I(00)$

Table S1c)

compound			EOE	THF	ACN
OO-DP	absorption analysis	$\nu_{\max}(\text{abs})$	19450	19000	18750
		Δf	0.1669	0.20957	0.30542
		$\nu_{00}(\text{abs})$	16830	16380	16130
		$\Delta\nu_{1/2}$	4800	5550	4900
	absorption fit	rel I (01) ^{a)}	2.6	2.48	2.41
		rel I (02) ^{b)}	3.32	3.03	2.89
		n_{abs}	2	2	2
		ν_{00}	16622	16264	15978
	fluorescence analysis	$\nu_{\max}(\text{fluo})$	14800	14700	13600
		$\nu_{00}(\text{fluo})$	16110	16010	14910
		n_{fluo}	1	1	1

a) $\text{rel I (01)} = I(01) / I(00)$, b) $\text{rel I (02)} = I(02) / I(00)$

Table S1d)

compound			EOE	EtOAc	THF	ACN
SO-DP ^{a)}	absorption analysis	$\nu_{\max}(\text{abs})$	19250	18600	18850	18700
		Δf	0.1669	0.19964	0.20957	0.30542
		$\nu_{00}(\text{abs})$	16630	15980	16230	16080
		$\Delta\nu_{1/2}$	4500	4600	4650	4850
		n_{abs}	2	2	2	2

a) Absorption spectra are unstructured and fluorescence is extremely weak: Peakfit absorption and fluorescence analysis could not be performed.

Table S2: Absorption and fluorescence characteristics of the acidic forms of the dyes (a – NOH-DP, b – NOH-DT, c – OOH-DP, d – SOH-DP) as a function of polarity (EOE, EtOAc, THF, ACN) obtained from experimental spectra (based on the solvatochromic spectral results for acidic forms in respective Figs. 3a,b,c,d of the main text); the notation is the same as in Table S1. Band fitting was not possible for the unstructured spectra.

Table S2a)

compound			EOE	EtOAc	THF	ACN
NOH-DP	absorption analysis	$v_{\max}(\text{abs})$	24700	24700	24200	24650
		Δf	0.1669	0.19964	0.20957	0.30542
		$v_{00}(\text{abs})$	22080	22080	21580	22050
		$\Delta v_{1/2}$	4100	4200	4450	4300
		n_{abs}	2	2	2	2
	fluorescence analysis	$v_{\max}(\text{fluo})$	18100	18100	18100	18000
		$\Delta v_{1/2}$	3300	3350	3050	2950
		$v_{00}(\text{fluo})$	20720	20720	20720	20600
		n_{fluo}	2	2	2	2

Table S2b)

compound			EOE	EtOAc	THF	ACN
NOH-DT	absorption analysis	$v_{\max}(\text{abs})$	23850	24000	23650	24050
		Δf	0.1669	0.19964	0.20957	0.30542
		$v_{00}(\text{abs})$	21230	21380	21030	21430
		$\Delta v_{1/2}$	5100	5250	5300	5250
		n_{abs}	2	2	2	2
	fluorescence analysis	$v_{\max}(\text{fluo})$	17800	17600	17500	17400
		$\Delta v_{1/2}$	3000	3050	3050	2950
		$v_{00}(\text{fluo})$	20420	20220	20120	20020
		n_{fluo}	2	2	2	2

Table S2c)

compound			EOE	THF	ACN
OOH-DP	absorption analysis	$v_{\max}(\text{abs})$ Δf $v_{00}(\text{abs})$ $\Delta v_{1/2}$ n_{abs}	19300 0.1669 17990 2950 1	19150 0.20957 17840 3750 1	19950 0.30542 18640 3100 1
	fluorescence analysis	$v_{\max}(\text{fluo})$ $\Delta v_{1/2}$ $v_{00}(\text{fluo})$ n_{fluo}	16600 1900 17910 1	16000 2300 17310 1	16200 2200 17510 1

Table S2d)

compound			EOE	EtOAc	THF	ACN
SOH-DP	absorption analysis	$v_{\max}(\text{abs})$ Δf $v_{00}(\text{abs})$ $\Delta v_{1/2}$ n_{abs}	18450 0.1669 17140 3200 1	18850 0.19964 17540 3200 1	18100 0.20957 16790 3050 1	19000 0.30542 17690 3250 1
	fluorescence analysis	$v_{\max}(\text{fluo})$ $\Delta v_{1/2}$ $v_{00}(\text{fluo})$ n_{fluo}	15300 1950 16610 1	15200 2065 16510 1	15000 1950 16310 1	15000 2150 16310 1

Appendix

General Concept of Electron Donor Ability Φ and Effective Length L of Residues in the Framework of the Long-Chain Approximation

The long-chain approximation is an analytical method using topological indices² to describe the electronic properties of chain-like polymethine compounds containing, in the general case, two end groups.³⁻⁵ The basic topological indices of end groups are electron donor ability Φ and effective length L .

The electron donor ability Φ of a residue is a characteristic of its donor/acceptor properties: it estimates the energy gap position relative to the Fermi level for a sufficiently long odd $(2n+1)$ -methine chain with two corresponding end groups. This quantity is defined as $F = 90^\circ \lim_{n \rightarrow \infty} [(E_{\text{LUMO}} - \alpha) / (E_{\text{LUMO}} - E_{\text{HOMO}})]$ where E_{HOMO} and E_{LUMO} are the energies of the highest occupied and lowest unoccupied molecular orbitals and $\alpha \equiv 0$ is the Coulomb integral of the C atom. Φ is measured in degrees so that its value ranges from 0° (for the least electron-donor residues with the nonbonding LUMO coinciding with the Fermi level) to 90° (for the most electron-donor residues with the nonbonding HOMO coinciding with the Fermi level).

The effective length L of a residue estimates the longest absorption wavelength of the above-described polymethine system as $(L + n) \cdot 100$ nm. L shows to what extent the first electronic transition of a sufficiently long odd $(2n+1)$ -methine chain is red-shifted when two corresponding end groups are bound to it. This dimensionless quantity is defined as $L = \lim_{n \rightarrow \infty} [\pi\beta / (E_{\text{HOMO}} - E_{\text{LUMO}}) - n]$ where $\beta \equiv -1$ is the resonance integral of the CC bond; the larger the L value of an end group, the closer to each other the frontier MOs are in the correspondingly terminated polymethine chain. In other words, the effective length L of a residue expresses its π -conjugation length, or “mesomeric box”, in terms of the equivalent amount of methine pairs (so-called vinylene groups).

Calculation of Φ and L of Residues by the Asymptotic Nonbonding MO Coefficients

As a linear conjugated system grows longer, its frontier MOs tend to come closer to each other and finally transform into a degenerated nonbonding MO (NBMO). This is how a notion of

an asymptotic NBMO can be introduced.³⁻⁵ The procedure for calculating asymptotic NBMO coefficients on end groups of a sufficiently long polymethine chain does not differ from that used for finding a “real”, or exact, NBMO.⁶ The set of NBMO coefficients C_q on a N -atomic conjugated residue is found as a solution of system of equations (1), with H_{pq} as Hamiltonian matrix elements (diagonal, $q = p$, implying atomic Coulomb integrals α_p and off-diagonal, $q \neq p$, implying bond resonance integrals β_{pq}):

$$\sum_{q=1}^N H_{pq} C_q = 0; p = 1, 2, \dots, N \quad (1A)$$

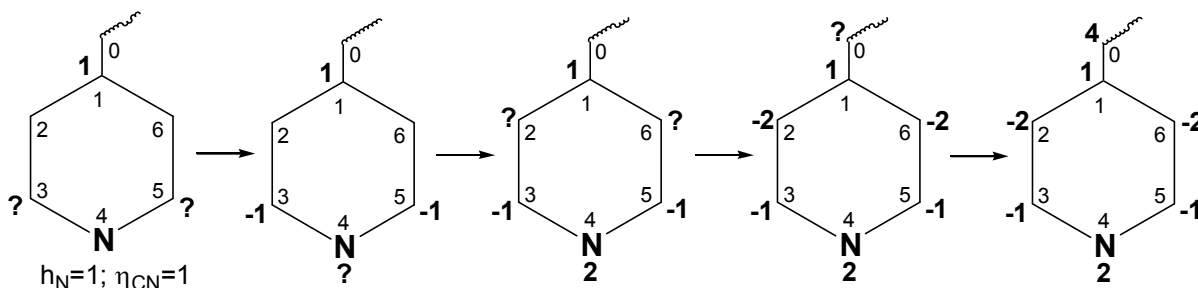
This system of equations has a single (trivial) solution, with all C_q equal to zero, for most of conjugated molecules. In general, odd alternant hydrocarbons (systems without odd-membered rings) are the only class of conjugated organics always possessing NBMO. Some exceptions occur among compounds of other classes. The concept of asymptotic NBMO provides a set of nonzero C_q values for an arbitrary conjugated residue.

Rewriting the corresponding equations for each p -th atom with the finite non-dimensional parameters h_p and η_{pq} ,

$$h_p C_p + \sum_{\substack{\text{over bonds} \\ q}} \eta_{pq} C_q = 0; \quad (2A)$$

$$h_p = (\alpha_p - \alpha) / \beta; \quad \eta_{pq} = \beta_{pq} / \beta; \quad \alpha = 0; \beta = -1$$

it is convenient to find the asymptotic NBMO coefficients by a simple non-computer “paper-and-pencil” technique⁶ and exemplified here by the 4-pyridinium end group (with the conventional values of the N atom topological parameters, $h_N = 1$, $h_{CN} = 1$ – see Ref. 7):



Conditions (2A) imposed on NBMO coefficients are satisfied for all atoms of the above system except the 0-th atom (the first atom of the polymethine chain); it is assumed that the

corresponding discrepancy can be cancelled elsewhere within the sufficiently long polymethine chain between the end groups (in view of the asymptotic nature of the NBMO found).

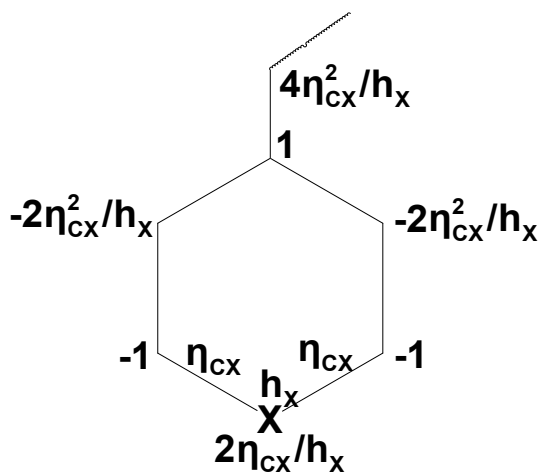
The electron donor ability Φ and effective length L of a residue are related, in a straightforward way, to NBMO coefficients on its atoms:

$$L = \left(2 \sum_{q=1}^N C_q^2 + C_0^2 \right) / (C_1^2 + C_0^2) \quad (3A)$$

$$F = \arctan(C_0 / C_1) \quad (4A)$$

For instance, the 4-pyridinium end group is characterized by $\Phi = \arctan(4/1) \approx 76^\circ$ and $L = [2 \cdot (4 \cdot 3 + 3) + 16] / (1 + 16) \approx 2.7$

Taking advantage of the simple structure of 4-X heterosubstituted phenyl group, it is possible to generalize the expressions for asymptotic NBMO coefficients on it and, accordingly, for electron donor ability and effective length in terms of h_x and η_{CX} , heteroatomic and heterobond parameters:

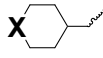


$$\Phi = \arctan \frac{4\eta_{CX}^2}{h_x} \quad (5A)$$

$$L = \frac{2(3h_x^2 + 16\eta_{CX}^4 + 4\eta_{CX}^2)}{h_x^2 + 16\eta_{CX}^4} \quad (6A)$$

Table 1A lists the electron donor ability and effective length calculated as the functions of h_x and η_{CX} parameters for the 4-X hetaryl as well as phenyl and 3-penta-1,3-dienylium groups. As seen, the Φ and L values for the hetero substituted phenyl ring approach those for the conjugated 5-

methine chain as the heteroparameter η_{CX} approaches zero (i.e., the heteroatom is gradually removed from the ring).

Table 1A: Electron donor ability Φ and effective length L for some six-membered (het)aryl groups  with the conventional values of h_X and η_{CX} parameters.⁷

X	h_X	η_{CX}	Φ (degrees)	L
N	1	1	76	2.7
O	2	0.8	52	4.0
S	0.7	0.4	42	5.6
Se	0.65	0.35	37	6.0
Any completely separated heteroatom thus yielding the 3-penta-1,3-dienylium group	Any $h_X \neq 0$	0	0	6.0
C	0	1	0	2.5

References

- (1) Program "peak-fit", v 4, AISN software Inc, 1995.
- (2) *Applications of Topological Methods in Molecular Chemistry*; Chauvin, R., Lepetit, C., Silvi, B., Alikhani, E., Eds. In: *Challenges and Advances in Computational Chemistry and Physics*, vol. 22. Springer International Publishing AG Switzerland: Basel, 2016.
- (3) Dyadyusha, G. G.; Kornilov, M. Yu.; Dekhtyar, M. L. On the application of the inverse adjacency matrix in HMO method. *J. Inf. Rec. Mater.* **1988**, *16*, 275-283.
- (4) Dyadyusha, G. G.; Kachkovsky, A. D.; Dekhtyar, M. L.. Colour and topology of conjugated systems. *J. Mol. Struct. (THEOCHEM)* **1990**, *217*, 195-206.
- (5) Dekhtyar, M. L. Application of the quasi-long chain approximation to structural perturbations of polymethine dyes. *Dyes Pigm.* **1995**, *28*, 261-274.
- (6) Dewar, M. J. S. A Molecular Orbital Theory of Organic Chemistry. *J. Am. Chem. Soc.* **1952**, *74*, 3341-3363.
- (7) Streitwieser, A. *Molecular Orbital Theory for Organic Chemists*; J. Wiley & Sons, Inc.: New York, 1961.