

Supporting Information for

Dual Character of Excited Radical Anions in Aromatic Diimide Bis(radical anion)s: Donor or Acceptor?

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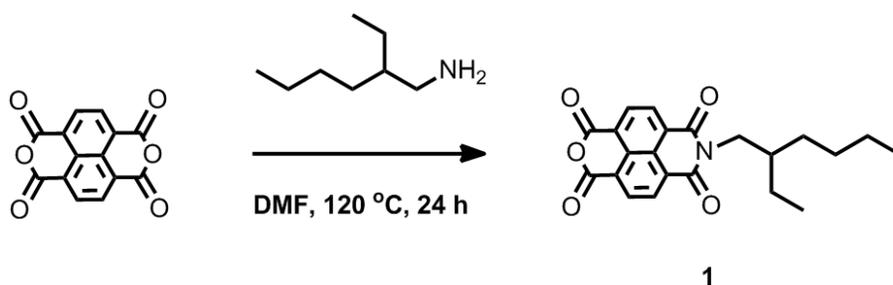
Synthesis procedures

N-(2-Ethylhexyl)naphthalenetetracarboxylic monoanhydride monoimide (**1**)

In a single-neck round-bottom flask equipped with a reflux condenser, 1,4,5,8-naphthalenetetracarboxylic dianhydride (6.18 g, 23.04 mmol) was suspended in 80 mL of DMF, and the solution was stirred at 80 °C. To this solution 2-ethyl-1-hexylamine (2.98 g, 23.06 mmol) was added drop wise over a period of 1 h and the mixture was heated to 120 °C under argon atmosphere. After 24 hours, the reaction mixture was cooled to room temperature and the precipitated diimide were filtered off. DMF was evaporated under reduced pressure. The crude material was purified by column chromatography (silica gel; dichloromethane) to obtain the pale yellow solid **1** (4.09 g, 10.78 mmol, 47%).

¹H NMR (CDCl₃, 400 MHz): δ 0.87 (t, *J* = 6.9 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H), 1.30 (m, 8H), 1.90 (m, 1H), 4.10 (m, 2H), 8.76 (m, 4H).

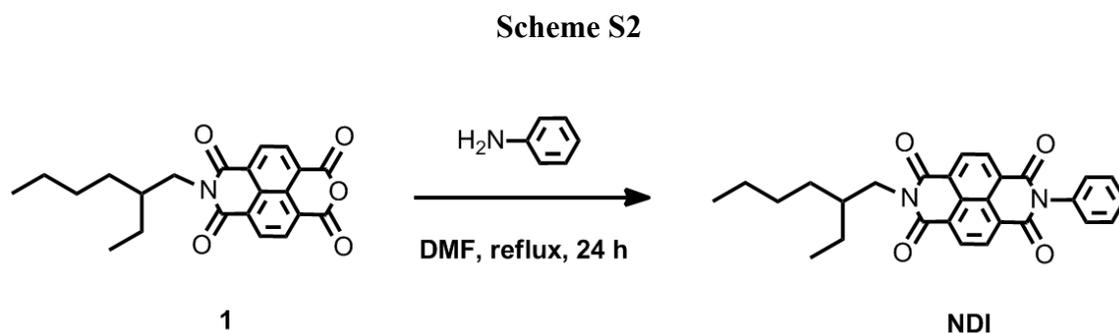
Scheme S1



NDI

1 (0.33 g, 0.87 mmol) and aniline (0.24 g, 2.58 mmol) were dissolved in 50 mL of DMF. The reaction mixture was heated with stirring to reflux for 24 h under argon atmosphere. Afterwards the reaction mixture was evaporated in vacuo and further purified by column chromatography (silica gel; dichloromethane) to obtain the pale yellow solid **NDI** (0.20 g, 0.44 mmol, 51%).

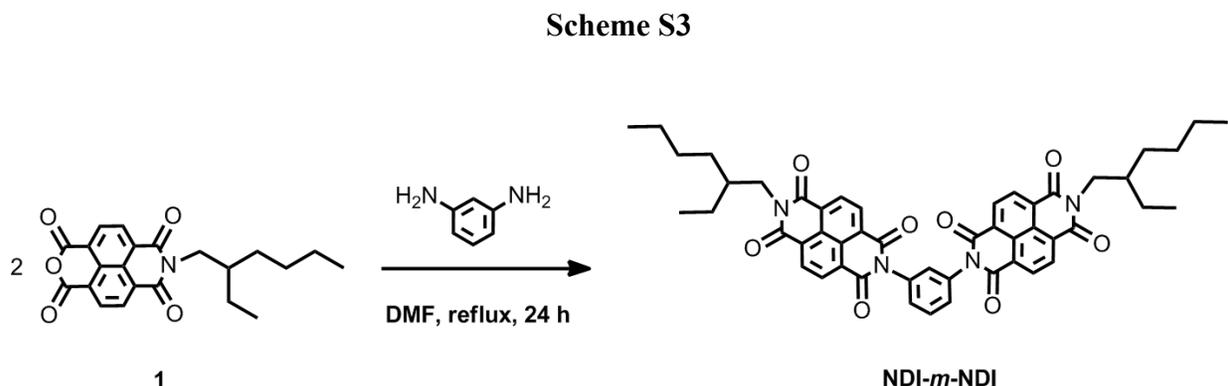
¹H NMR (CDCl₃, 400 MHz): δ 0.87 (t, *J* = 7.3 Hz, 3H), 0.94 (t, *J* = 7.8 Hz, 3H), 1.31 (m, 8H), 1.93 (m, 1H), 4.12 (m, 2H), 7.32 (m, 2H), 7.51 (m, 3H), 8.81 (m, 4H).



NDI-*m*-NDI

1 (0.61 g, 1.61 mmol) and *m*-phenylenediamine (0.09 g, 0.83 mmol) were dissolved in 50 mL of DMF. The reaction mixture was heated with stirring to reflux for 24 h under argon atmosphere. Afterwards the reaction mixture was evaporated in vacuo and purified by column chromatography (silica gel; chloroform and then chloroform/ethyl acetate (gradient)). Further purification was carried by column chromatography (silica gel; dichloromethane and then dichloromethane/ethyl acetate (gradient)) to obtain the pale yellow solid **NDI-*m*-NDI** (30 mg, 0.04 mmol, 5%).

^1H NMR (CDCl_3 , 400 MHz): δ 0.87 (t, $J = 7.3$ Hz, 6H), 0.93 (t, $J = 7.8$ Hz, 6H), 1.31 (m, 16H), 1.94 (m, 2H), 4.11 (m, 4H), 7.39 (m, 1H), 7.51 (m, 2H), 7.77 (m, 1H), 8.79 (m, 8H). FAB MS: calcd. 830.33, found 831 (M+1).

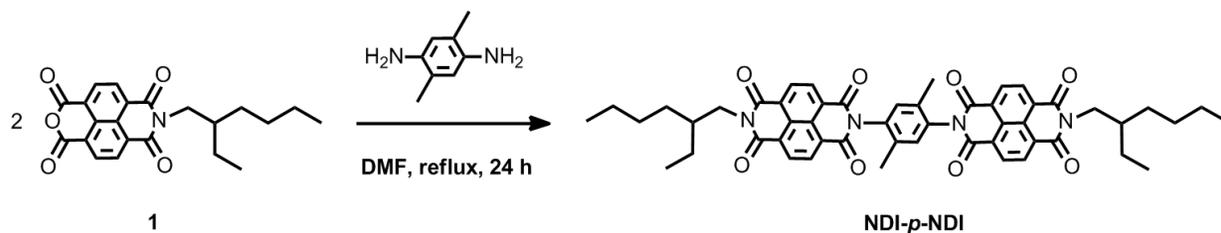


NDI-*p*-NDI

1 (0.89 g, 2.35 mmol) and 2,5-dimethylbenzene-1,4-diamine (0.16 g, 1.17 mmol) were dissolved in 50 mL of DMF. The reaction mixture was heated with stirring to reflux for 24 h under argon atmosphere. Afterwards the reaction mixture was evaporated in vacuo and purified by column chromatography (silica gel; chloroform and then chloroform/ethyl acetate (gradient)). Further purification was carried by column chromatography (silica gel; dichloromethane and then dichloromethane/ethyl acetate (gradient)) to obtain the pale yellow solid **NDI-*p*-NDI** (50 mg, 0.06 mmol, 5%).

^1H NMR (CF_3COOH , 400 MHz): δ 0.85 (t, $J = 7.1$ Hz, 6H), 0.95 (t, $J = 7.3$ Hz, 6H), 1.28 (m, 16H), 2.03 (m, 2H), 2.23 (m, 6H), 4.32 (m, 4H), 7.43 (m, 2H), 8.98 (m, 8H). FAB MS: calcd. 858.36, found 859 (M+1).

Scheme S4



Kinetic traces

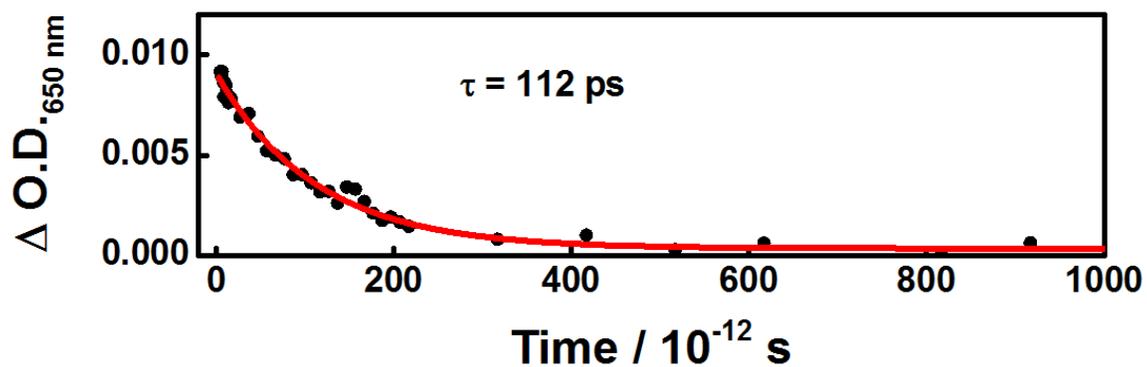


Figure S1. Kinetic trace of $\Delta O.D.$ at 650 nm during the 475 nm laser flash photolysis of NDI (0.20 mM) in DMF in the presence of TDAE (0.20 mM).

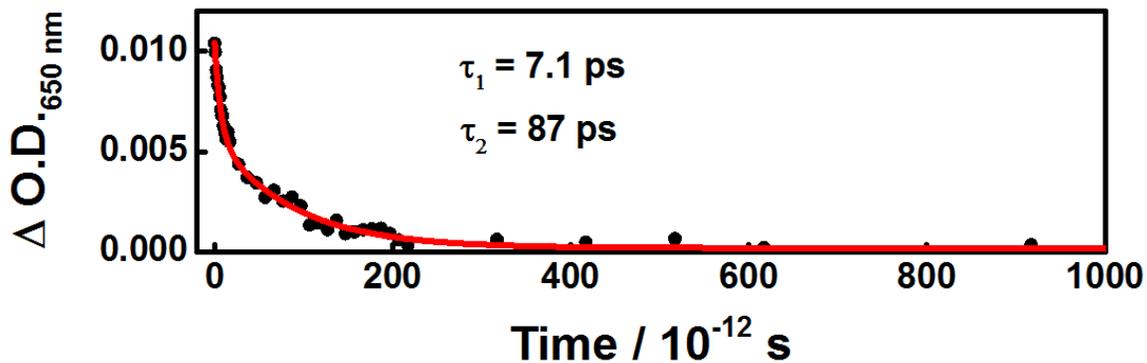


Figure S2. Kinetic trace of $\Delta \text{O.D.}$ at 650 nm during the 475 nm laser flash photolysis of NDI *-m*-NDI (0.20 mM) in DMF in the presence of TDAE (0.40 mM).

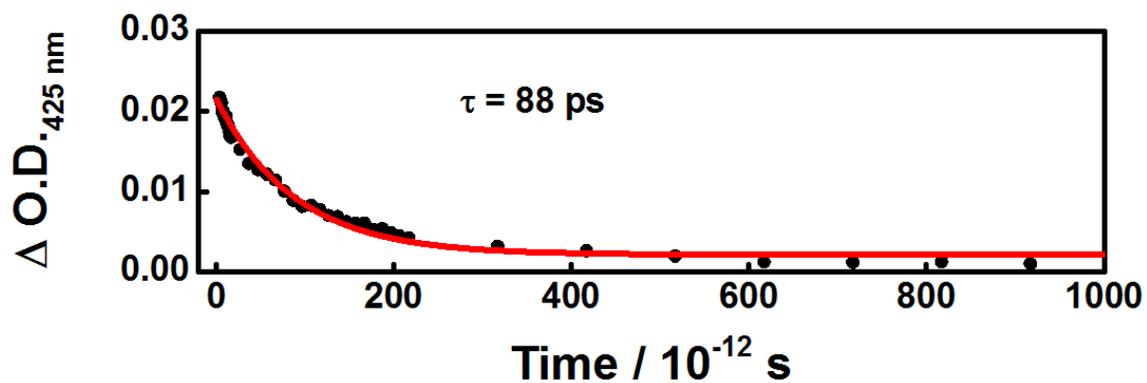


Figure S3. Kinetic trace of $\Delta \text{O.D.}$ at 425 nm during the 475 nm laser flash photolysis of NDI *-m*-NDI (0.20 mM) in DMF in the presence of TDAE (0.40 mM).

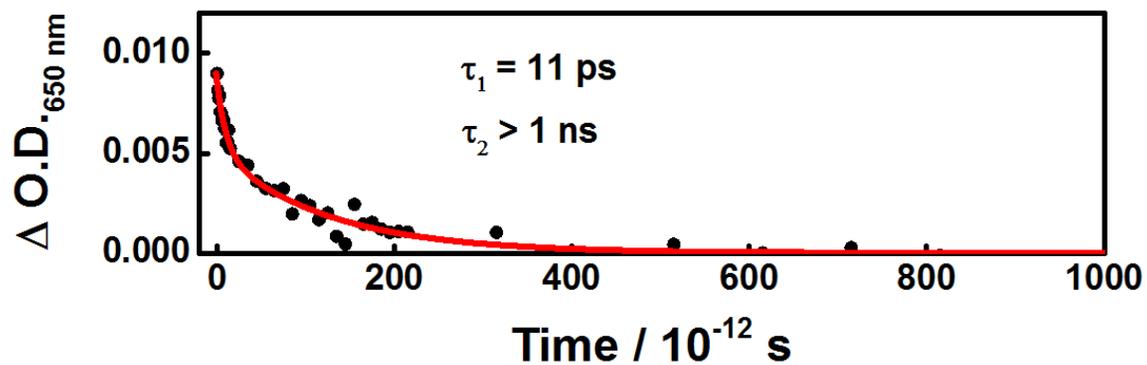


Figure S4. Kinetic trace of $\Delta O.D.$ at 650 nm during the 475 nm laser flash photolysis of NDI -*p*-NDI (0.20 mM) in DMF in the presence of TDAE (0.40 mM).

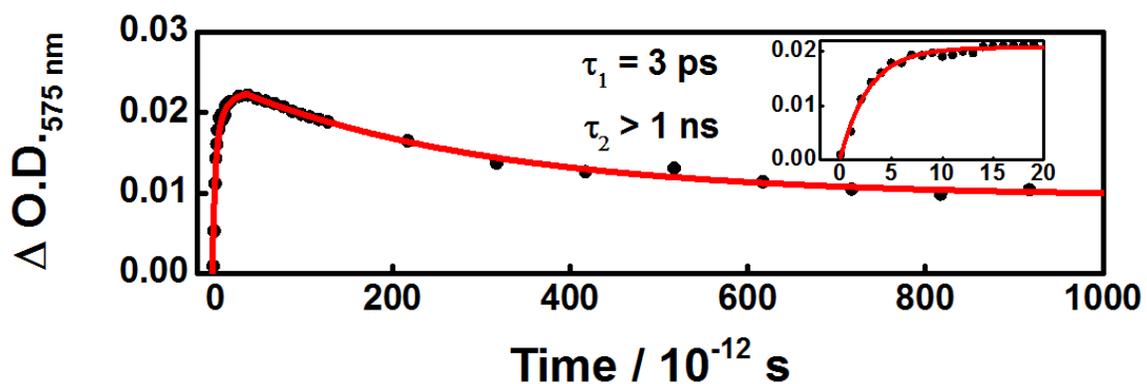


Figure S5. Kinetic trace of $\Delta O.D.$ at 575 nm during the 475 nm laser flash photolysis of NDI -*m*-PDI (0.20 mM) in DMF in the presence of TDAE (0.40 mM). (Inset: enlarged kinetic trace within 20 ps.)

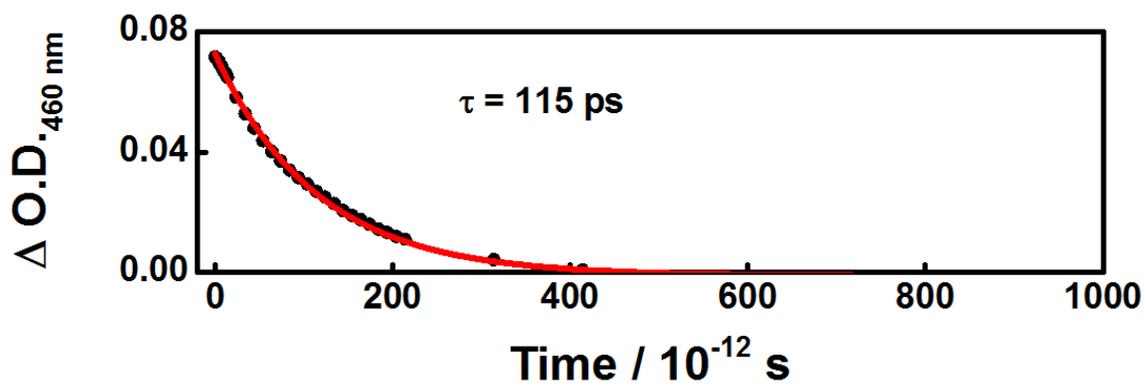


Figure S6. Kinetic trace of Δ O.D. at 460 nm during the 700 nm laser flash photolysis of NDI *-m*-PDI (0.12 mM) in DMF in the presence of TDAE (0.24 mM).

Global analysis

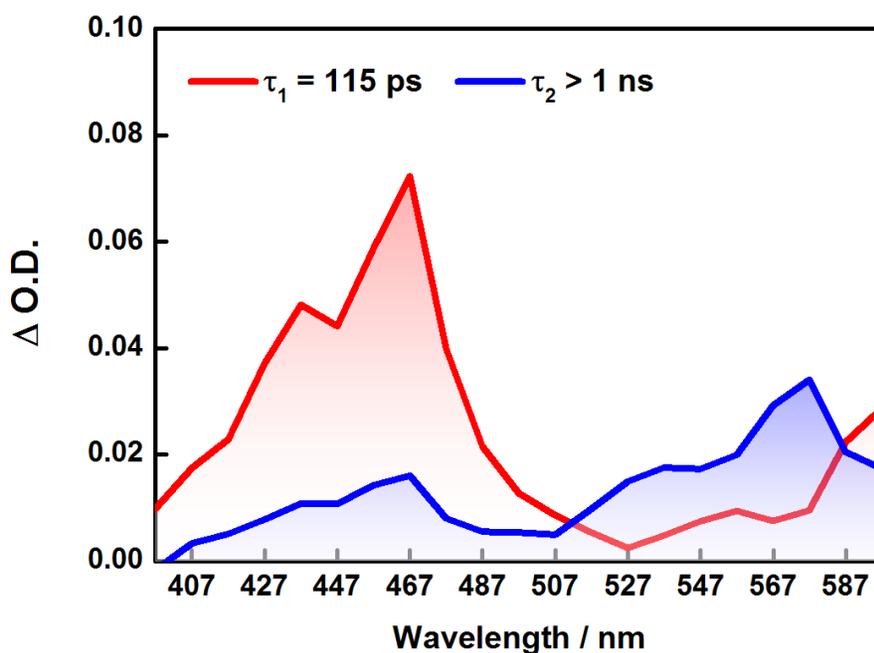


Figure S7. Species-associated spectra obtained by global analysis on the absorption band (400-600 nm) in Figure 4b.