Tuning the reorganization energy of electron transfer in supramolecular ensembles – metalloporphyrin, oligophenylenevinylene, and fullerene – and the impact on electron transfer kinetics

Christina Stangel¹, Christina Schubert³, Susanne Kuhri³, Georgios Rotas², Johannes T. Margraf³,⁴, Elżbieta Regulska³, Timothy Clark⁴, Tomás Torres⁶,⁷, Nikos Tagmatarchis²*, Dirk M. Guldi³*, Athanassios G. Coutsolelos¹*

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Figure S2: Upper part – differential absorption spectra (visible) obtained upon pump probe excitation (420 nm, 200 nJ) of ZnTPP in chlorobenzene with several time delays between 0.1 and 6750 ps at room temperature – see legend for details. Lower part – time-absorption profiles of the spectra in chlorobenzene at 460, 555, 577, and 700 nm monitoring the excited state dynamics.
Synthetic details and characterization

Scheme S1. Reagents and conditions: a) $\text{C}_{12}\text{H}_{25}\text{Cl}$, KOH, EtOH, reflux, 12 h, 93%; b) paraformaldehyde, HBr, 65 °C, 15 h, 98%; c) NaHCO$_3$, DMSO, 115 °C, 0.5 h, 45%, d) PPh$_3$, toluene, reflux, 3 h; e) (i) 4, LiOEt, CH$_2$Cl$_2$, room temperature, 10 min; (ii) I$_2$, CH$_2$Cl$_2$, room temperature, overnight, 81.2%.
Scheme S2. Reagents and conditions: a) triethylphosphite, 140 °C, 48 h, 85%; b) 2,2- dimethylpropane-1,3-diol,p-TsOH (cat.), benzene, reflux, Dean-Stark trap, 24 h, 82.3%; c) (i) 11, tBuOK, THF, 0 °C, 2 h; (ii) I₂, CH₂Cl₂, H₂O, room temperature, overnight, 80%; d) CF₃CO₂H, CH₂Cl₂, H₂O, room temperature, 4 h, 93%.
1,4-Bis(dodecyloxy)benzene (8). A suspension of 1,4 hydroquinone (10 g, 90.8 mmol), 1-chlorododecane (63 mL, 272.4 mmol) and KOH (15 g, 267.3 mmol), in ethanol (200mL), under N\textsubscript{2} was heated at reflux overnight. The reaction mixture was cooled to room temperature and the precipitates were filtered and washed with ethanol and water. After being dried under vacuum the precipitates dissolved in hot methanol. Reprecipitation of resulting solution in methanol then gave 8 as a white solid, after being filtered and dried under vacuum (37.7 g, 93% yield).

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta 0.89 (t, J = 7 Hz, 6H), 1.26 (m, 32H), 1.44 (m, 4H), 1.78 (quintet, J = 7Hz, 4H), 3.89 (t, J = 6.5 Hz, 4H), 6.82 (s, 4H).

\textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta 153.36, 115.56, 68.84, 32.06, 29.80, 29.74, 29.73, 29.56, 29.55, 26.20, 22.8, 14.2.

HRMS (MALDI-TOF): \(m/z\) calcd for C\textsubscript{30}H\textsubscript{54}O\textsubscript{2}: 446.4125 [M]+. Found: 446.4117.

2,5-Bis(bromomethyl)-1,4-bis(dodecyloxy)benzene (9). To a suspension of 8 (6 g, 13.43 mmol) and paraformaldehyde (0.806 g, 26.86mmol) in acetic acid (44 mL), HBr (6.0 mL, 33 wt % in acetic acid) was added and the mixture was heated to 65 – 70 °C for 15 h. The resulting solution was cooled to room temperature and water was added (400 mL). The precipitates were filtered, washed with water, dried under vacuum and then dissolved in hot methylene chloride. Reprecipitation of resulting solution in methanol then gave 9 as a white solid after being filtered and dried under vacuum (8.338 g, 98% yield).

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta 0.88 (t, J = 6.9 Hz, 6H), 1.26 (m, 32H), 1.48 (m, 4H), 1.80 (m, 4H,) 3.98 (t, J = 6.6 Hz, 4H), 4.52 (s, 4H), 6.84 (s, 4H).

\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta 150.84, 127.70, 114.84, 69.20, 32.90, 26.22, 22.85, 14.28.

HRMS (MALDI-TOF): \(m/z\) calcd for C\textsubscript{32}H\textsubscript{56}Br\textsubscript{2}O\textsubscript{2}: 630.2647 [M]+. Found: 630.2653.

2,5-Bis(dodecyloxy)benzene-1,4-dialdehyde (4). A suspension of 9 (2 g, 3.162 mmol) and NaHCO\textsubscript{3} (4 g, 47.43 mmol) in dimethyl sulfoxide (50 mL) was heated at 115 °C for 0.5 h before being poured into water (500 mL). The yellow precipitate was filtered, washed with water and dried under vacuum. The residue was purified by column chromatography (SiO\textsubscript{2}, hexanes/CH\textsubscript{2}Cl\textsubscript{2}, 1:1) to obtain 4 as a yellow fluorescent solid. (0.715 g, 45% yield).

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta 0.88 (t, J = 6.9 Hz, 6H), 1.26 (m, 32H), 1.48 (m, 4H), 1.80 (m, 4H,) 3.98 (t, J = 6.6 Hz, 4H), 4.52 (s, 4H), 6.84 (s, 4H).

\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta 189.57, 155.38, 129.44, 111.,7 69.40, 32.40, 29.74, 26.15, 22.82, 14.24.

HRMS (MALDI-TOF): \(m/z\) calcd for C\textsubscript{32}H\textsubscript{54}O\textsubscript{4}: 502.4022 [M]+. Found: 502.4030.

2,5-Bis(dodecyloxy)-1,4-bis[(2,5-didecoxy-4-formyl)phenylenevinylene] benzene (3). A suspension of 9 (0.576 g, 1.0 mmol) and triphenylphosphine (0.26 g, 0.99 mmol) in dry toluene, under N\textsubscript{2} was heated at reflux for 3 h. The solvent was then removed under reduced pressure and the resulting residue being dried. Dialdehyde 4 (0.47 g, 0.94 mmol) was then added, and the resulting residue dissolved in dry methylene chloride (24 mL). To this solution lithium ethoxide solution (1.18 mL, 1.0 M in ethanol) was added
dropwise at room temperature. The base should be introduced at such a rate that the transient red-purple color produced upon the addition of base should not persist. The reaction was quenched by the addition of dilute aqueous HCl. The organic layer was separated, washed with water, dried (Na$_2$SO$_4$), filtered and concentrated. The resulting residue contained both $E$- and $Z$-isomers. A solution of the $E:Z$ isomer mixture and I$_2$ (500 mg) in methylene chloride (50 mL) was stirred at room temperature overnight. The dark brown solution was then diluted with methylene chloride and washed consecutively with aqueous Na$_2$S$_2$O$_3$ solution (1.0 M, 2 x 75 mL). The organic layer was washed with water, dried (Na$_2$SO$_4$), filtered and evaporated to dryness. Column chromatography (SiO$_2$, CH$_2$Cl$_2$/ hexane, 6:4) gave 3 as an orange fluorescent solid (0.55 g, 81.2 % yield).

{[(2,5-bis(dodecyloxy)-1,4-phenylene]bis(methylene)}bis-tetraethylphosphonate (11). A mixture of 9 (0.6 g, 1.10 mmol) and triethylphosphite (1.9 mL, 11 mmol) was heated at 150 °C for 24h. After cooling to room temperature, the excess of triethylphosphite was distilled under reduced pressure at 70 °C. Reprecipitation of resulting glassy product in petroleum ether then gave 11 as a white solid, after being filtered and dried under vacuum (0.69 g, 85%).$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 0.87 (t, $J$ = 6.3 Hz, 6H), 1.23 (m, 44H), 1.44 (m, 4H), 1.75 (m, 4H), 3.21 (d, $J$$_{PH}$ = 20.4 Hz, 2H), 3.90 (t, $J$ = 6.6 Hz, 4H), 4.02 (dq, $J$$_{PH}$ = 7.2 Hz, $J$$_{HH}$ = 7.2 Hz, 8H), 6.9 (s, 2H).$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 189.84, 156.17, 150.25, 134.73, 125.37, 112.19, 110.36, 96.67, 69.26, 26.28, 22.83, 16.53, 16.50, 16.48, 14.26. HRMS (MALDI-TOF): $m/z$ calcd for C$_{40}$H$_{76}$O$_8$P$_2$: 746.5015 [M]$^+$ Found: 746.5021.

4-[(5,5-dimethyl-1,3-dioxan-2-yl)-2,5-bis(dodecyloxy)]benzaldehyde (12). A solution of 4 (0.11 g, 0.23 mmol), 2,2-dimethylpropane-1,3-diol (0.025 g, 0.26 mmol), and $p$-TsOH (1 mg, 0.0052 mmol) in benzene (6 mL) was refluxed for 48 h using a Dean-Stark trap. After cooling to room temperature, the solution was evaporated to dryness. The resulting residue was taken up in CH$_2$Cl$_2$. The organic layer washed with water, dried (Na$_2$SO$_4$), filtered and evaporated to dryness. Column chromatography (SiO$_2$, hexanes/CH$_2$Cl$_2$ 1:1) gave 12 (0.112 g, 82.3%) as a colorless solid.$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 0.78 (s, 1H), 0.88 (t, $J$ = 6.3 Hz, 6H), 1.26 (m, 35H), 1.44 (m, 4H), 1.78 (m, 4H), 3.66 (d, $J$ = 10.2 Hz, 2H), 3.76 (d, $J$ = 11.1 Hz, 2H), 3.98 (t, $J$ = 6.6 Hz, 2H), 4.08 (t, $J$ = 6.6 Hz, 2H), 5.73 (s, 1H), 7.30 (s, 1H), 10.46 (s, 1H).$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 189.84, 156.17, 150.25, 134.73, 125.37, 112.19, 110.36, 96.67, 69.26, 32.06, 30.51, 29.05,
2.2'-{(1E,1'E)-(2,5-bis(dodecyloxy)-1,4-phenylene)bis(ethene-2,1-diyl)}bis(2,5-bis(dodecyloxy)-4,1-phenylene)bis(5,5-dimethyl-1,3-dioxane) (13): t-BuONa (0.010 g, 0.09 mmol) was added to a solution of 11 (0.029 g, 0.038 mmol) and 12 (0.056 g, 0.077 mmol) in dry THF under N₂ at 0 °C. The mixture was stirred for 2 h and then the resulting solution evaporated to dryness. The residue was taken up with CH₂Cl₂. The organic layer washed with water, dried (Na₂SO₄), filtered and evaporated to dryness. The resulting residue contained both E and Z isomers. Isomerization to the all E- isomers was achieved following the procedure as described for compound 3. Column chromatography (SiO₂, CH₂Cl₂ /hexane, 8:2) gave 13 (0.049 g, 80%) as a yellow fluorescent solid.

1H NMR (300 MHz, CDCl₃): δ 0.80 (s, 1H), 0.87 (m, 18H), 1.28 (m, 102H), 1.52 (m, 12H), 1.80 (m, 12H), 3.67 (d, J = 10.8 Hz, 4H), 3.77 ( d, J = 10.8 Hz, 4H), 4.01 (m, 12H), 5.75 (s, 2H), 7.13 (m, 4H), 7.18 (s, 2H), 7.45 (s, 1H).

13C NMR (125 MHz, CDCl₃):δ 151.20, 150.48, 128.74, 127.46, 127.13, 123.89, 123.55, 111.65, 110.74, 110.70, 97.28, 78.05, 69.64, 69.52, 32.08, 30.45, 29.89, 29.86, 29.72, 29.64, 29.53, 26.46, 26.39, 26.33, 23.40, 22.84, 22.05, 14.27. HRMS (MALDI-TOF): m/z calcd for C₁₁₀H₁₈₂O₁₀: 1615.3733 [M]+. Found: 1615.3726.

2,5-Bis(dodecyloxy)-1,4-bis[(2,5-didecoxy-4-formyl)phenylenevinylene] benzene (3). A mixture of 13 (0.030 g, 0.018 mmol) and CF₃CO₂H (0.6 mL) in CH₂Cl₂/H₂O 1:1 (2 mL) was stirred at room temperature for 4 h. The organic layer was washed with water, dried (Na₂SO₄), filtered and evaporated to dryness. Column chromatography (SiO₂, CH₂Cl₂ / hexane, 6:4) gave 6 as an orange fluorescent solid (0.025 g, 93% yield).
$^1$H NMR and $^{13}$C NMR for all the new compounds

**Figure S3a.** $^1$H-NMR spectrum in CDCl$_3$ of compound 8.
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