Supporting Information for

Excitation energy migration in oligo(*p*-phenylenevinylene) based organogels: Structure-property relationship and FRET efficiency

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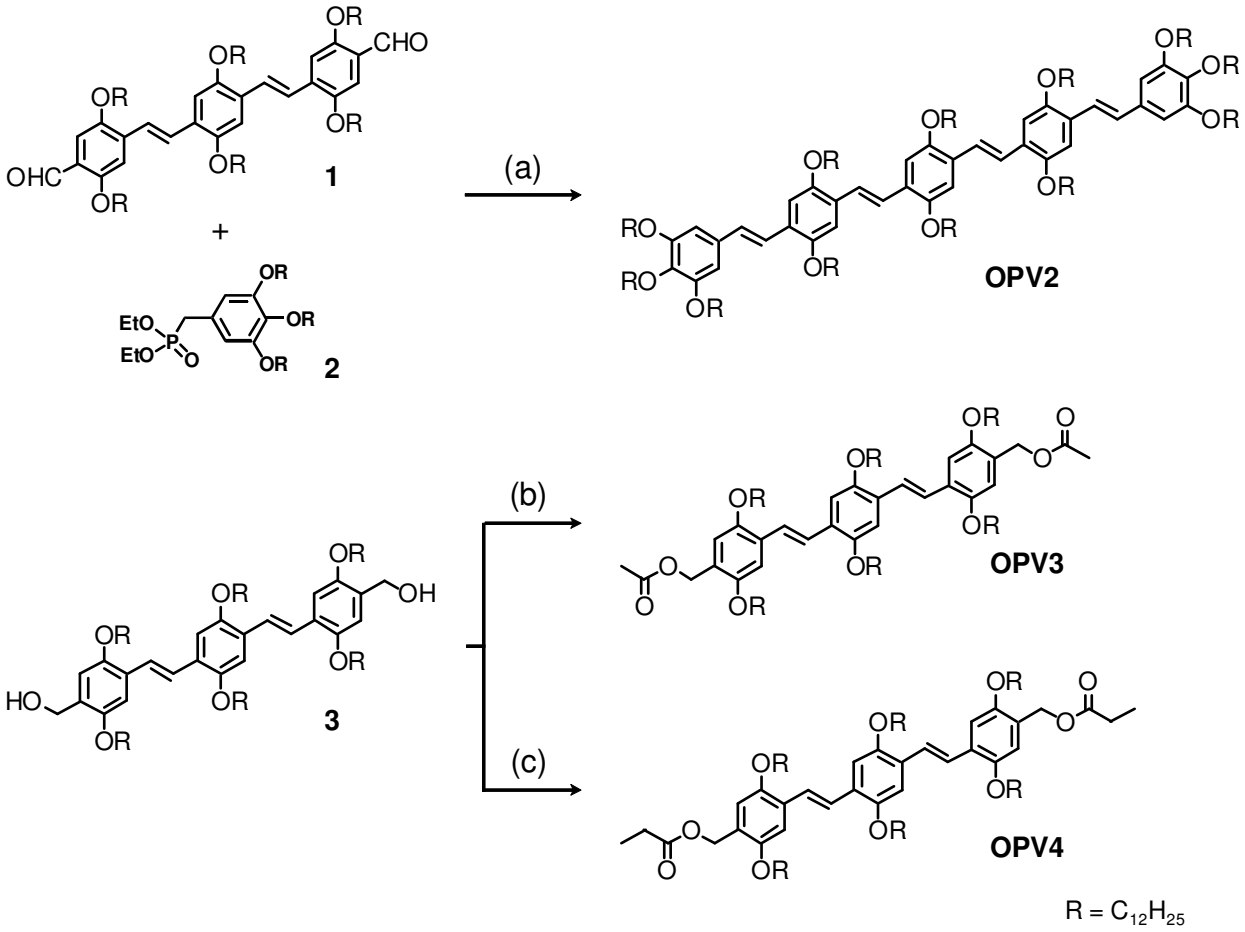
1. Synthesis and characterization

Syntheses of **OPV1** and **OPV5** were reported earlier.[S1] **OPV2-4** were prepared as per Scheme 1. The starting compounds OPV bisaldehyde (**1**), OPV bisalcohol (**3**) and tridodecyloxybenzene (**2**) derivatives were synthesized as per reported procedures.[S2]



Scheme 1 Synthesis of **OPV2-4**. Reagents and conditions: (a) NaH, THF, 60 °C, 12 h, 70%; (b) acetic acid, DCC, DMAP, CH_2Cl_2, 0 °C - rt, 4 h, 97%; (b) propionic acid, DCC, DMAP, CH_2Cl_2, 0 °C - rt, 4 h, 96%.

*Synthesis of **OPV2**:* Compound **1** (144 mg, 0.1 mmol) was dissolved in anhydrous THF (10 mL) by stirring under argon atmosphere at room temperature. Compound **2** (195 mg, 0.25 mmol, 2.5 equiv.) dissolved in THF (10 mL) along with NaH (40 mg, 1 mmol) was added drop-wise to the stirring solution from a pressure equalizer. After the addition, the reaction temperature was

slowly raised to 60 ºC and stirred at that temperature for 12 h. The reaction mixture was then cooled to room temperature and quenched with ice. Solvent was evaporated and the residue was extracted with chloroform for three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel/1:3 chloroform-hexane) followed by precipitation from THF by the addition of methanol.

Mp 103-105 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.82 (s, 36H), 0.91-2.38 (m, 192H), 3.90-4.05 (m, 24H), 6.88 (s, 2H), 7.07 (s, 4H), 7.22 (s, 8H), 7.53 (s, 4H), 7.68 (s, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.34, 13.98, 19.56, 20.95, 22.64, 22.90, 24.28, 25.58, 27.62, 28.20, 28.78, 28.95, 29.32, 29.52, 29.61, 29.61, 29.72, 31.71, 32.11, 32.23, 36.19, 36.72, 37.31, 37.42, 37.99, 39.88, 40.14, 42.62, 49.72, 56.64, 56.88, 63.72, 68.27, 69.51, 76.46, 108.73, 114.34, 116.18, 124.41, 126.86, 127.56, 128.21, 133.21, 138.93, 142.73, 154.63, 155.84, 155.95 ppm. FT-IR (KBr): ν_{max} 698, 725, 791, 857, 949, 969, 1002, 1032, 1077, 1208, 1261, 1352, 1379, 1423, 1462, 1503, 2850, 2922 cm^{-1}. MALDI-TOF MS (MW = 2696.43): m/z = 2696.46 [M^+].

*General procedure for the synthesis of **OPV3-4**:* Compound **3** (145 mg, 0.1 mmol) was dissolved in anhydrous CH_2Cl_2 (20 mL) by stirring under argon atmosphere at room temperature. Acetic acid (24 mg, 0.4 mmol) or propionic acid (30 mg, 0.4 mmol) and catalytic amount of DMAP were added to the stirring solution. The reaction mixture was then cooled to 0 ºC by using a salt-ice bath. After 10 minutes, DCC (83 mg, 0.4 mmol) was added to the reaction mixture and continued stirring for 4 h while the temperature was allowed to rise to the room temperature. The reaction mixture was poured in to water and extracted with chloroform for three times. The combined extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by column chromatography

(silica gel/1:3 chloroform-hexane) followed by precipitation from THF by the addition of methanol.

OPV3: Mp 88-90 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.79-0.81 (m, 18H), 1.18-1.26 (m, 96H), 1.34-1.42 (m, 12H), 1.66-1.79 (m, 12H), 2.11 (s, 6H), 3.89-4.00 (m, 12H), 5.15 (s, 4H), 6.90 (s, 2H), 7.13 (s, 4H), 7.46 (s, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.42, 21.34, 22.98, 26.50, 26.54, 26.63, 29.67, 29.78, 29.86, 29.97, 30.00, 32.22, 62.06, 69.10, 69.66, 69.89, 96.43, 109.85, 110.89, 115.40, 123.59, 124.23, 124.59, 127.64, 128.53, 150.76, 151.36, 151.65, 170.98 ppm. FT-IR (KBr): ν_{max} 688, 721, 759, 803, 856, 898, 932, 967, 1025, 1066, 1122, 1208, 1252, 1335, 1382, 1426, 1465, 1506, 1591, 1718, 2852, 2921 cm^{-1}. MALDI-TOF MS (MW = 1531.28): m/z = 1531.23 [M^+].

OPV4: Mp 87-89 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.78-0.82 (m, 18H), 0.96 (s, 6H) 1.14-1.25 (m, 96H), 1.33-1.40 (m, 12H), 1.64-1.78 (m, 12H), 2.10 (s, 4H), 3.90-4.00 (m, 12H), 5.14 (s, 4H), 6.88 (s, 2H), 7.11 (s, 4H), 7.44 (s, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.33, 21.32, 22.92, 26.39, 26.50, 26.55, 26.62, 29.61, 29.70, 29.86, 29.79, 30.57, 32.15, 62.12, 69.33, 69.68, 69.77, 96.45, 109.16, 110.79, 117.46, 122.87, 123.47, 123.63 126.95, 127.65, 150.72, 151.28, 151.55, 171.02 ppm. FT-IR (KBr): ν_{max} 689, 722, 763, 802, 858, 900, 931, 969, 1024, 1068, 1124, 1210, 1252, 1333, 1381, 1427, 1463, 1504, 1592, 1719, 2853, 2922 cm^{-1}; MALDI-TOF MS (MW = 1559.31): m/z = 1559.36 [M^+].

2. Supporting figures

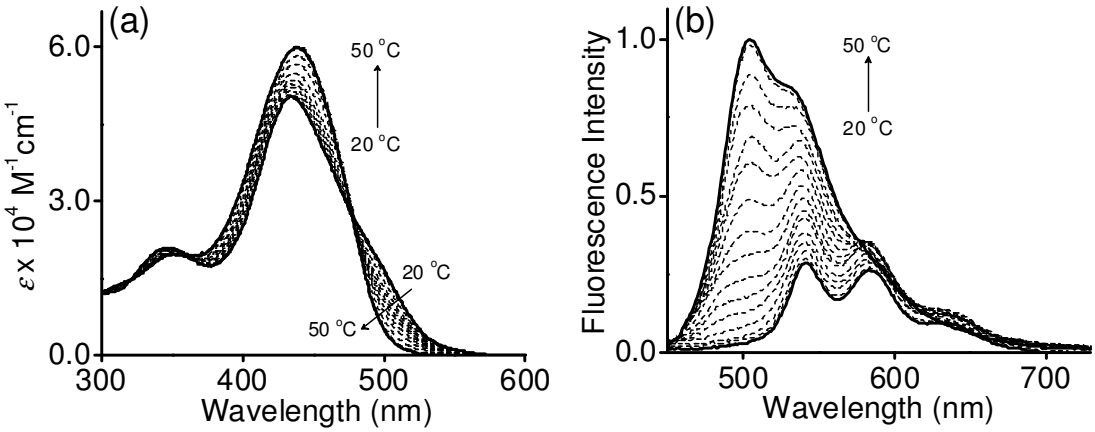


Fig. S1 Temperature dependent (a) absorption and (b) emission spectral changes of **OPV2** in *n*-decane. $c = 3 \times 10^{-4}$ M, $l = 1$ mm, $\lambda_{ex} = 420$ nm.

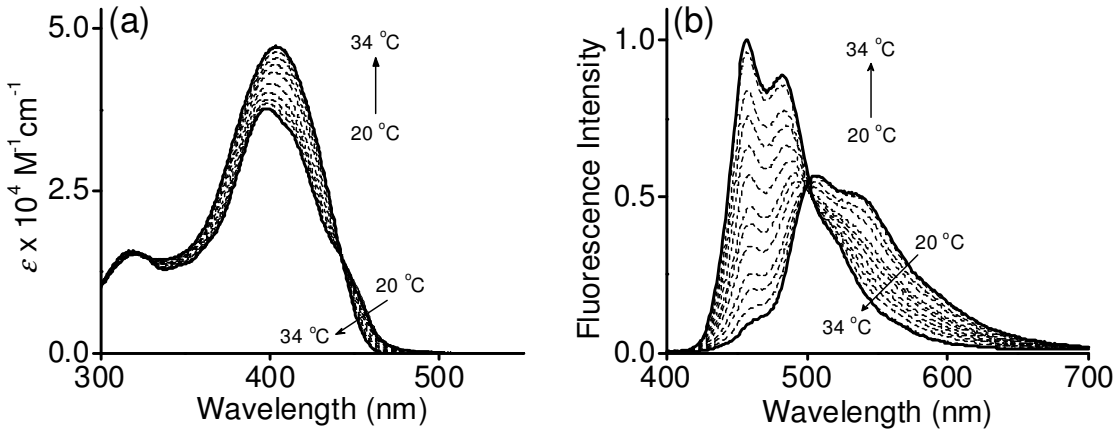


Fig. S2 Temperature dependent (a) absorption and (b) emission spectral changes of **OPV3** in *n*-decane. $c = 3 \times 10^{-4}$ M, $l = 1$ mm, $\lambda_{ex} = 380$ nm.

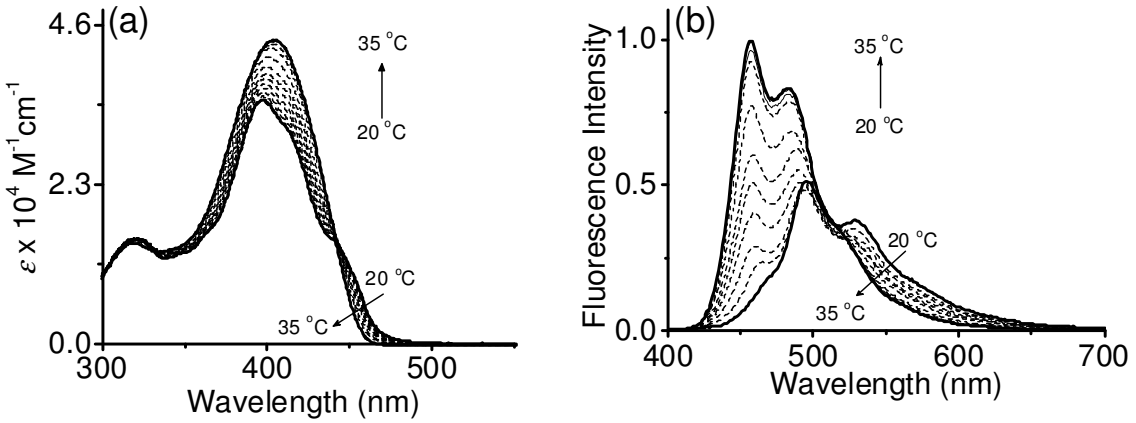


Fig. S3 Temperature dependent (a) absorption and (b) emission spectral changes of **OPV4** in *n*-decane at room temperature. $c = 3 \times 10^{-4}$ M, $l = 1$ mm, $\lambda_{ex} = 380$ nm.

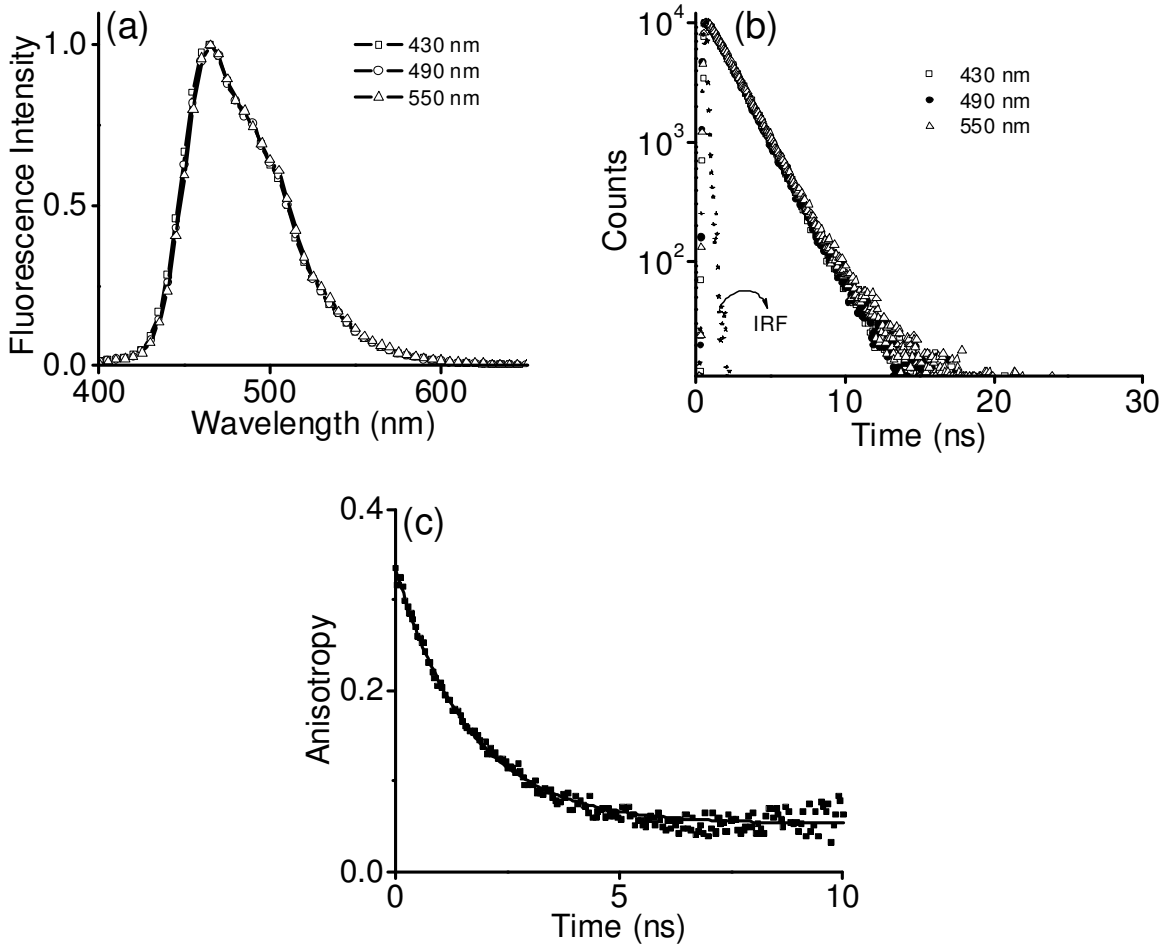


Fig. S4 (a) Time-resolved emission spectra, (b) wavelength dependent fluorescence decay and (c) fluorescence anisotropy decay of **OPV1** in chloroform at room temperature. $c = 3 \times 10^{-4}$ M, $l = 1$ mm, $\lambda_{ex} = 375$ nm.

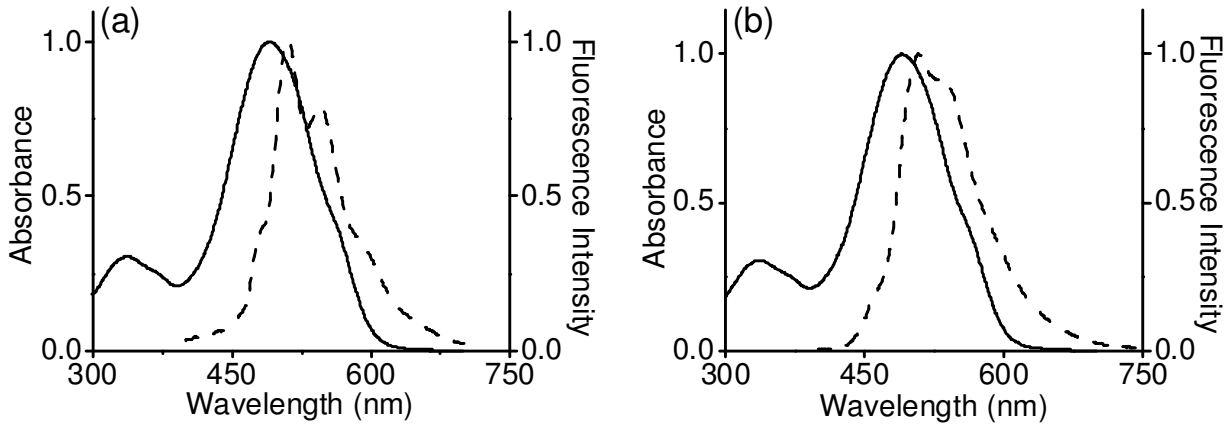


Fig. S5 Spectral overlap of the absorption (——) of **OPV5** and emission (– – –) of (a) **OPV1** and (b) **OPV3** in *n*-decane at room temperature (conc. of donor = 3×10^{-4} M, conc. of acceptor = 9.3×10^{-6} M, l = 1 mm, λ_{ex} = 380 nm).

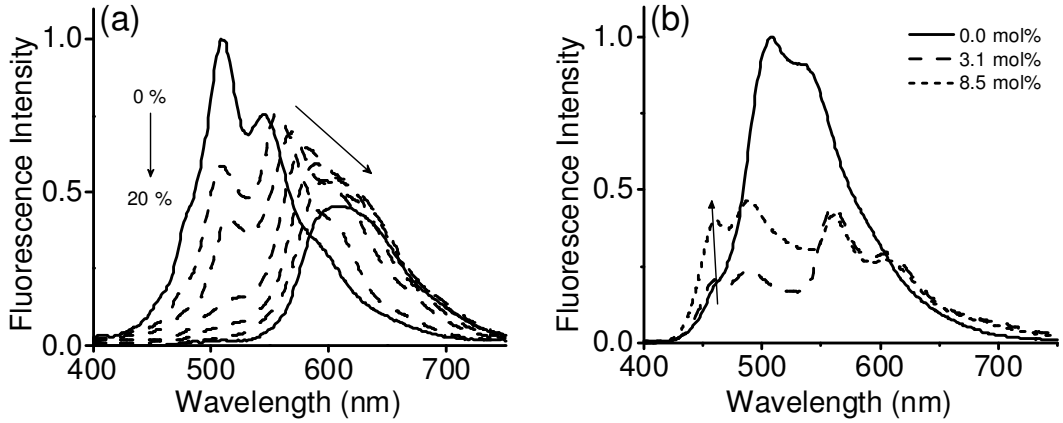


Fig. S6 Fluorescence spectral changes of (a) **OPV1** and (b) **OPV3** in presence various amounts of **OPV5** in *n*-decane at room temperature (conc. of donor = 3×10^{-4} M, l = 1 mm, λ_{ex} = 380 nm).

3. Calculation of spectral overlap integral

The spectral overlap integral $J(\lambda)$ of the donor emission and the acceptor absorption was calculated using equation 1.[S3]

$$J(\lambda) = \frac{\int_0^\infty F_D(\lambda)\, \varepsilon_A(\lambda)\, \lambda^4\, d\lambda}{\int_0^\infty F_D(\lambda)\, d\lambda} \qquad \text{- - - - - - - - (1)}$$

Where $F_D(\lambda)$ is the fluorescence intensity of the donor in the wavelength range λ to $\lambda+\Delta\lambda$, $\varepsilon_A(\lambda)$ is the extinction coefficient of the acceptor at λ.

4. Calculation of energy transfer rate constant

Rate of energy transfer (k_{ET}) was determined by using the following equation, which provides a lower limit for energy transfer rate.[S4]

$$k_{ET} = \frac{Q_{max} - 1}{\tau_D} \qquad \text{- - - - - - - - (2)}$$

Where $Q_{max} = I_D/I_{DA}$, is the maximum quenching observed in the fluorescence titration studies. τ_D is the average lifetime of the donor which is calculated by the following equation.[S3]

$$\langle\tau\rangle = \frac{\alpha_1\tau_1^2 + \alpha_2\tau_2^2}{\alpha_1\tau_1 + \alpha_2\tau_2} \qquad \text{- - - - - - - - (3)}$$

5. Supporting references

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S2. (*a*) A. Ajayaghosh and S. J. George, *J. Am. Chem. Soc*., 2001, **123**, 5148; (*b*) S. J. George and A. Ajayaghosh, *Chem. Eur. J*., 2005, **11**, 3217. (*c*) T. M. Figueira-Duarte, J. Clifford, V. Amendola, A. Gégout, J. Olivier, F. Cardinali, M. Meneghetti, N. Armaroli and J.-F. Nierengarten, *Chem. Commun.*, 2006, 2054.

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