

SUPPORTING INFORMATION

Very large acceleration of the photoinduced electron transfer in a Rubpy₃-naphthalene bisimide dyad bridged on the naphthyl core

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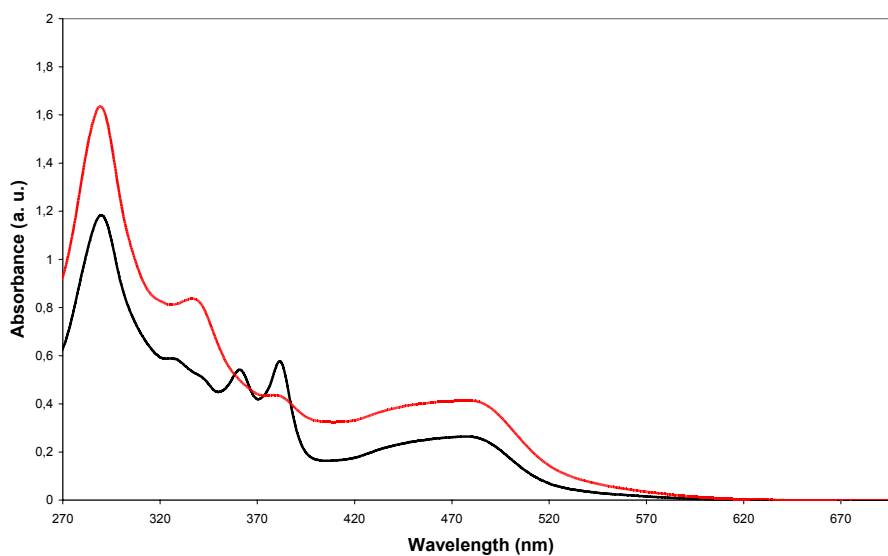


Figure S1 : Electronic absorption spectra of dyads **1** (red) and **2** (black) recorded in DMF

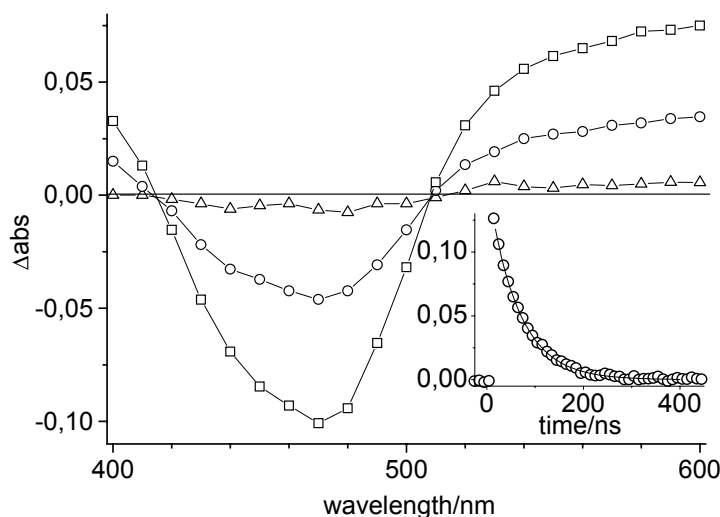


Figure S2. Transient absorption spectra for **2** recorded after 50 ns (squares), 100 ns (circles) and 250 ns (triangles). The inset shows the times resolved emission recorded at 650 nm. The solid line shows a single exponential fit with a time constant of 63 ns. (CH_3CN , 298K)

General Methods

^1H and ^{13}C NMR spectra were recorded on a Bruker ARX 300 MHz or AMX 400 MHz Bruker spectrometer. Chemical shifts for ^1H NMR spectra are referenced relative to residual protium in the deuterated solvent (CDCl_3 $\delta = 7.26$ ppm, MeOD $\delta = 3.31$ ppm). Mass spectra were recorded on a EI-MS HP 5989A spectrometer or on a JMS-700 (JEOL LTD, Akishima, Tokyo, Japan) double focusing mass spectrometer of reversed geometry equipped with electrospray ionization (ESI) source. Fast atom bombardment mass spectroscopy (FAB-MS) analyses were performed in m-nitrobenzyl alcohol matrix (MBA) on a ZAB-HF-FAB spectrometer. MALDI-TOF analyses were performed on an Applied Biosystems Voyager DE-STR spectrometer in positive linear mode at 20 kV acceleration voltage with a-cyano 4-hydroxycinnamic acid (CHCA) as matrix.

Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with Merck 5735 Kieselgel 60F254. Column chromatography was carried out either with Merck 5735 Kieselgel 60F (0.040-0.063 mm mesh) or with SDS neutral alumina (0.05-0.2 mm mesh). Air sensitive reactions were carried out under argon in dry solvents and glassware. Chemicals were purchased from Aldrich and used as received. Compounds 4-bromobipyridine^{S1}, bis-chloro bis-4,4'-dimethyl-bipyridine ruthenium(II)^{S2}, dibromoisocyanuric acid^{S3}, bis-chloro(diphenylphosphino)ferrocene palladium(II)^{S4}, N-octylnaphthalenetetracarboxylic-1,8-

anhydride-4,5-acid monoimide (**4**)^{S5}, 4'-trimethylsilylethynyl-trimethyltinbenzene (**13**)^{S6} and 2,5-bis(dodecyl)ethynylbenzene^{S7} were prepared according to literature methods.

The electrochemical measurements were performed with a potentiostat-galvanostat MacLab model ML160 controlled by resident software (Echem v1.5.2 for Windows) using a conventional single-compartment three-electrode cell. The working electrode was a Pt wire of 10 mm long, the auxiliary was a Pt wire and the reference electrode was the saturated potassium chloride calomel electrode (SCE). The supported electrolyte was 0.15 N Bu₄NPF₆ in dichloromethane and the solutions were purged with argon before the measurements. All potentials are quoted relative to SCE. In all the experiments the scan rate was 100 mV/s for cyclic voltammetry and 15 Hz for pulse voltammetry. UV-Visible absorption spectra were recorded on a UV-2401PC Shimadzu spectrophotometer. Fluorescence spectra were recorded on a SPEX Fluoromax fluorimeter and were corrected for the wavelength dependent response of the detector system. Time-resolved emission, and femtosecond and nanosecond transient absorption experiments were performed as described before.⁴

N-octyl-N'-(4'-iodophenyl)naphthalene-1,4,5,8-tetracarboxylic acid bisimide: 6

Compound **4** (820 g, 2.19 mmol) was dissolved in dimethylformamide (20 mL) and the solution was stirred at reflux. 4-iodoaniline **5** (0.959 g, 4.38 mmol) in dry dimethylformamide (5 mL) was added dropwise and the solution was heated for 15 hours. The reaction mixture was diluted in dichloromethane and washed with water. The organic layer was dried over MgSO₄, and rotary evaporated. The crude product was purified by flash column chromatography over silica gel (eluent : petroleum ether/dichloromethane 7/3). **6** was obtained as a yellow solid (0.606 g, 48 %).

¹H NMR (300 MHz, CDCl₃) : δ = 8.80 (s, 4H), 7.91 (d, J = 8.7 Hz, 2H), 7.08 (d, J = 8.7 Hz, 2H), 4.21 (m, 2H), 1.76 (m, 2H), 1.42 (m, 2H), 1.27 (m, 8H), 0.87 (m, 3H). ¹³C NMR (300 MHz, CDCl₃) : δ = 162.76, 162.66, 138.77, 134.29, 131.46, 131.00, 130.43, 127.09, 127.01, 126.81, 126.42, 94.97, 41.08, 31.79, 29.69, 29.27, 28.07, 27.08, 22.63, 14.08. EI-MS *m/z* : 580.15 (M⁺) (100 %), 469.05 (41 %), 249.05 (13 %).

N-octyl-N'-(4'-trimethylsilylethynylphenyl)naphthalene-1,4,5,8-tetracarboxylic acid bisimide : 7

A solution of compound **6** (150 mg, 0.26 mmol) in triethylamine (7 mL) and tetrahydrofuran (5 mL) was degassed with argon by pump/freeze cycles in a sealed tube. Then,

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PdCl₂ (4.6 mg, 0.026 mmol), Cu(OAc)₂ (2.6 mg, 0.013 mmol), PPh₃ (10 mg, 0.039 mmol) and trimethylsilylacetylene (0.09 mL, 0.65 mmol) were added. The reaction mixture was heated at 70°C for 15 hours. The solvents were rotary evaporated. The crude product was purified by flash column chromatography over silica gel (eluent : dichloromethane/petroleum ether 8/2). **7** was obtained as a yellow solid (129 mg, 90 %).

¹H NMR (300 MHz, CDCl₃) : δ = 8.79 (s, 4H), 7.65 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 4.20 (m, 2H), 1.75(m, 2H), 1.41(m, 2H), 1.27 (m, 8H), 0.87 (m, 3H), 0.27 (s, 9H). **¹³C NMR (300 MHz, CDCl₃)** : δ = 162.81, 162.71, 134.41, 133.02, 131.40, 131.01, 128.50, 127.04, 126.53, 96.05, 41.07, 31.79, 29.69, 29.27, 28.07, 27.08, 22.63, 14.08, -0,10. **EI-MS *m/z*** : 550.45 (M⁺) (55 %), 535.45 (100 %), 452.25 (2 %).

N-octyl-N'-(4'-ethynylphenyl)naphthalene-1,4,5,8-tetracarboxylic acid bisimide: 8

Compound **7** (82 mg, 0.15 mmol) was dissolved in tetrahydrofuran (13 mL) and the flask was purged with argon. Then tetrabutylammonium fluoride (1.2 mmol) was added and the reaction mixture was stirred at room temperature for 1 hour. The solvent was rotary evaporated and water was added. The solution was extracted with dichloromethane and the organic layer was washed with water, dried over MgSO₄ and rotary evaporated. **8** was obtained as a yellow solid (71 mg, quantitative).

¹H NMR (300 MHz, CDCl₃) : δ = 8.78 (s, 4H), 7.68 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 4.14 (m, 2H), 3.17 (s, 1H), 1.75(m, 2H), 1.41(m, 2H), 1.27 (m, 8H), 0.87 (m, 3H).

2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic dianhydride: 11

A solution of 1, 4, 5, 8-naphthalenetetracarboxylic dianhydride **9** in sulphuric acid (6 mL) (1 g, 3.73 mmol) was slowly added to a solution of dibromoisocyanuric acid **10** (2.1 g, 7.49 mmol) in sulphuric acid (6 mL) and the resulting mixture was stirred at 130°C for 15 hours. The reaction mixture was poured onto ice and the resulting precipitate was filtered and washed with water. **11** was obtained as a yellow solid (1.58 g, quantitative).

¹H NMR (300 MHz, DMSO) : δ = 11.65 (s, 4H), 8.79 (s, 2H). **¹³C NMR (300 MHz, DMSO)** : δ = 157.90, 156.39, 137.51, 135.87, 129.38, 127.40, 124.19. **EI-MS *m/z*** : 648.20 (M⁺) (43 %), 568.25 (28 %), 490.40 (28 %).

N,N'-dioctyl-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid bismide: 12

Compound **11** (0.5 g, 1.09 mmol) was dissolved in acetic acid (40 mL) and the solution was heated at 130°C. Then n-octylamine (0.72 mL, 4.35 mmol) was added and the solution was heated for one hour. Then the reaction mixture was poured onto ice and the resulting precipitate is filtered and washed with water. The crude product was purified by flash column chromatography over alumina (eluent :petroleum ether/dichloromethane/methanol starting with the composition 2/8/0 until 0/9/1). **12** was obtained as a salmon solid (200 mg, 28 %).

¹H NMR (300 MHz, CDCl₃) : δ = 8.98 (s, 2H), 4.17 (m, 4H), 1.70 (m, 4H), 1.21 (m, 20H), 0.87 (m, 6H). **EI-MS *m/z*** : 648.20(M⁺) (43 %), 568.25 (28 %), 490.40 (28 %).

N,N'-dioctyl-2,6-(4'-triméthylsilylethynylphenyl)naphthalene-1,4,5,8-tetracarboxylic acid bismide: 14

A solution of compound **13** (78 mg, 0.23 mmol), **12** (50 mg, 0.077 mmol) in dry toluene (3 mL) was introduced in a sealed tube and degassed by pump/froze cycles. Then Pd(PPh₃)₄ (4.5 mg, 0.004 mmol) was added. The reaction mixture was heated at 120°C for 15 hours. The solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography over silica gel (eluent : petroleum ether/dichloromethane starting with the composition 8/2 until 5/5). **14** was obtained as a yellow solid (49 mg, 76 %).

¹H NMR (300 MHz, CDCl₃) : δ = 8.61 (s, 2H), 7.61 (d, J = 8.1 Hz, 4H), 7.34 (d, J = 8.1 Hz, 4H), 4.05 (m, 4H), 1.63 (m, 4H), 1.30 (m, 20H), 0.86 (m, 6H), 0.28 (s, 18H). **¹³C NMR (300 MHz, CDCl₃)** : δ = 162.38, 162.13, 146.39, 140.49, 135.50, 132.01, 128.05, 127.25, 125.67, 123.39, 122.94, 104.84, 95.63, 41.07, 31.80, 29.72, 29.29, 28.03, 27.06, 22.65, 14.12, 0.00. **EI-MS *m/z*** : 834.20 (M⁺) (27 %), 721.90 (2 %), 608.90 (11 %).

N,N'-dioctyl-2,6-(4'-ethynylphenyl)naphthalene-1,4,5,8-tetracarboxylic acid bismide: 15

Compound **14** (45 mg, 0.054 mmol) was dissolved in tetrahydrofuran (5 mL) and the flask was purged with argon. Tetrabutylammonium fluoride (0.16 mL, 0.16 mmol) was added and the reaction mixture was stirred at room temperature for 1 hour. The solvent was rotary evaporated and water was added. The solution was extracted with diethylether and the organic layer was washed with water, dried over MgSO₄ and rotary evaporated. **15** was obtained as a yellow solid (37 mg, quantitative).

¹H NMR (300 MHz, CDCl₃) : δ = 8.61 (s, 2H), 7.65 (d, J = 8.1 Hz, 4H), 7.37 (d, J = 8.1 Hz, 4H), 4.04 (m, 4H), 3.15 (s, 2H), 1.63 (m, 4H), 1.30 (m, 20H), 0.86 (m, 6H). **EI-MS *m/z*** : 690.15 (M⁺) (4 %), 579.10 (29 %), 465.95 (21 %).

Dyad 1

A solution of compound **15** (37 mg, 0.054 mmol), **16** (53 mg, 0.054 mmol) in dry triethylamine (0.8 mL) and dimethylformamide (5.2 mL) was introduced in a sealed tube and degassed by pump/froze cycles. Pd(dppf)Cl₂ (8.1 mg, 0.011 mmol) and CuI (2 mg, 0.011 mmol) were added and the reaction mixture was heated at 70°C for 15 hours. Water was added and the solution was extracted with dichloromethane. The organic layer was then washed with water, dried over MgSO₄, and rotary evaporated. The crude product was purified by flash column chromatography over silica gel (eluent : acetonitrile/water/saturated aqueous solution of KNO₃ starting with the composition 80/20/0 until 78/20/2). **1** was obtained as a red solid (24 mg, 40 %).

¹H NMR (300 MHz, CD₃CN) : δ = 8.63 (s, 2H), 8.51 (m, 4H), 8.35 (m, 8H), 8.06 (m, 2H), 7.75 (m, 8H), 7.61 (m, 2H), 7.54 (m, 6H), 7.44 (m, 8H), 7.23 (m, 8H), 3.98 (m, 4H), 2.53 (s, 24H), 1.59 (m, 4H), 1.25 (m, 20H), 0.83 (m, 6H). **HRMS-ES⁺ *m/z*** : calcd for C₁₁₄H₁₀₆N₁₄O₄Ru₂ 484.6652; found 484.6667 M⁴⁺.

Dyad 2

A solution of compound **16** (80 mg, 0.082 mmol), **8** (50 mg, 0.010 mmol) in triethylamine (0.8 mL) and dimethylformamide (5.2 mL) was introduced in a sealed tube and degassed by pump/froze cycles. Pd(dppf)Cl₂ (16 mg, 0.021 mmol) and CuI (4 mg, 0.021 mmol) were added and the reaction mixture was heated at 45°C for 15 hours. Water was added and the solution was extracted with dichloromethane. The organic layer was then washed with water, dried over MgSO₄, and rotary evaporated. The crude product was purified by flash column chromatography over silica gel (eluent : dichloromethane/acetonitrile starting with the composition 100/0 until 95 / 5). **2** was obtained as a red solid (53 mg, 47 %).

¹H NMR (300 MHz, CD₃CN) : δ = 8.67 (s, 4H), 8.63 (m, 1H), 8.53 (m, 1H), 8.36 (m, 4H), 8.06 (m, 1H), 7.79 (m, 4H), 7.62 (m, 1H), 7.53 (m, 3H), 7.45 (m, 4H), 7.25 (m, 4H), 4.10 (m, 2H), 2.54 (s, 12H), 1.71 (m, 2H), 1.37 (m, 2H), 1.28 (m, 8H), 0.86 (m, 3H). **¹³C NMR (300 MHz, CD₃CN)** : δ = 164.21, 163.95, 158.67, 157.80, 157.58, 157.54, 157.47, 152.69, 151.95, 151.68, 151.59, 151.47, 139.66, 138.56, 138.34, 133.91, 132.56, 131.74, 131.50, 130.73,

129.51, 129.35, 128.80, 128.30, 127.90, 126.85, 125.99, 125.95, 122.77, 87.34, 41.62, 37.88, 36.91, 36.62, 32.63, 30.07, 30.01, 28.69, 27.89, 23.44, 21.35, 14.46. **HRMS-ES m/z** : calcd for $C_{64}H_{56}N_8O_4Ru$ 551.1734; found 551.1745 M^{2+} .

Reference complex 3

A solution of compound **16** (50 mg, 0.050 mmol), **2,5-bis(dodecyl)ethynylbenzene** (35 mg, 0.075 mmol) in triethylamine (0.15 mL) and dimethylformamide (1 mL) was introduced in a sealed tube and degassed by pump/froze cycles. $Pd(dppf)Cl_2$ (7.5 mg, 0.010 mmol) and CuI (1.9 mg, 0.010 mmol) were added and the reaction mixture was heated at 45°C for 15 hours. Water was added and the solution was extracted with dichloromethane. The organic layer was then washed with water, dried over $MgSO_4$, and rotary evaporated. The crude product was purified by flash column chromatography over silica gel (eluent :dichloromethane/acetonitrile starting with the composition 100/0 until 90/10). **3** was obtained as a red solid (49 mg, 70 %).

1H NMR (300 MHz, CD_3CN) : δ = 8.67 (s, 4H), 8.63 (m, 1H), 8.53 (m, 1H), 8.36 (m, 4H), 8.06 (m, 1H), 7.79 (m, 4H), 7.62 (m, 1H), 7.53 (m, 3H), 7.45 (m, 4H), 7.25 (m, 4H), 4.10 (m, 2H), 2.54 (s, 12H), 1.71 (m, 2H), 1.37 (m, 2H), 1.28 (m, 8H), 0.86 (m, 3H). **^{13}C NMR (300 MHz, CD_3CN)** : δ = 164.21, 163.95, 158.67, 157.80, 157.58, 157.54, 157.47, 152.69, 151.95, 151.68, 151.59, 151.47, 139.66, 138.56, 138.34, 133.91, 132.56, 131.74, 131.50, 130.73, 129.51, 129.35, 128.80, 128.30, 127.90, 126.85, 125.99, 125.95, 122.77, 87.34, 41.62, 37.88, 36.91, 36.62, 32.63, 30.07, 30.01, 28.69, 27.89, 23.44, 21.35, 14.46. **HRMS-ES+ m/z** : calcd for $C_{64}H_{56}N_8O_4Ru$ 551.1734; found 551.1745 M^{2+} .

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