Supporting information to:

Photoinduced intercomponent excited-state decays in a molecular dyad made of a dinuclear rhenium(I) chromophore and a fullerene electron acceptor unit

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Materials, equipments, and methods

All reagents were obtained from commercial suppliers and used without further purification; where needed, solvents were deoxygenated and dried by standard methods. 4-(Pyridazin-4-yl)-butanoic acid, complex **2** and fulleropyrrolidine **3** were prepared according to literature procedures.[1] [60]Fullerene was purchased from Bucky-USA. All reactions involving the rhenium complexes were performed using the Schlenk technique. Flash-chromatography was performed over SiO_2 (Macherey-Nagel 60 M, 0.04-0.063 μm, 230-400 mesh for derivatives **3-5**; 70-230 mesh for dyad **1**. ^{1}H and ^{13}C NMR spectra were recorded at 301 K on a Bruker AC-300, AC-500 or AC-250 instruments using the partially deuterated solvent as the internal reference. The multiplicity of a signal is indicated as: br - broad, s - singlet, d - doublet, t - triplet, q - quartet, m - multiplet, dd - doublet of doublets, dt - doublet of triplets, etc. FT-IR absorption spectra were recorded with a Nicolet 5700 FT-IR spectrophotometer or on a Bruker Vector22 FT instrument. Atmospheric pressure photoionization mass spectroscopy (APPI-MS) was performed in a ESI-TOF Mariner™ Biospectrometry™ Workstation of Applied Biosystems by direct infusion of a cyclohexane solution. Preparative HPLC was performed on a Shimadzu LC-8A equipped with a UV detector at 340 nm and a Buckyprep column, using toluene as eluent at a rate of 8mL/min. UV/Vis absorption spectra were recorded with a Jasco V-560 and Varian Cary 5000 and Cary 100 spectrophotometers. For steady-state luminescence measurements, a Jobin Yvon-Spex Fluoromax P spectrofluorimeter was used, equipped with a Hamamatsu R3896 photomultiplier. The spectra were corrected for photomultiplier response using a program purchased with the fluorimeter. For the luminescence lifetimes, an Edinburgh OB 900 time-correlated single-photon-counting spectrometer was used. A Hamamatsu PLP 2 laser diode (59 ps pulse width at 408 nm) and/or nitrogen discharge (pulse width 2 ns at 337 nm) were employed as excitation sources. Emission quantum yields for deaerated solutions were determined by the optically diluted method[2] with [Ru(bpy)$_3$]$^{2+}$ (bpy = 2,2'-bipyridine) in air equilibrated aqueous solution as quantum yield standard (Φ_{em} = 0.028).[3]

Time-resolved transient absorption experiments were performed using a pump–probe setup based on the Spectra-Physics MAI-TAI Ti:sapphire system as the laser source and the Ultrafast Systems Helios spectrometer as the detector. The pump pulse was generated using a Spectra-Physics 800 FP OPA instrument. The probe pulse was obtained by continuum generation on a sapphire plate (spectral range 450–800 nm). The effective time resolution was around 200 fs, and the temporal chirp over the white-light 450–750 nm range around 150 fs; the temporal window of the optical delay stage was 0–3200 ps. NIR extension to the multichannel pump-probe transient absorption spectrometer was used for the near-infrared experiments. A fiber optics coupled multichannel spectrometer with InGaAs sensor have been used as NIR detector. The extension allows for probing

the photoinduced transients in the 800-1600 nm range, with 3.5 nm intrinsic resolution (sensitivity range: 800-1600 nm; maximum spectral acquisition rate- 7900 spectra/s). In order to cancel out orientation effects on the dynamics, the polarization direction of the linearly polarized probe pulse was set at a magic angle of 54.7 ° with respect to that of the pump pulse. Please note that all the transient spectra shown in the present paper are chirp corrected. The chirp correction was done by using the pump induced absorption signals themselves in the same conditions (same cuvette, solvent, temperature, stirring frequency…) used for each single experiment. All the time-resolved data were analyzed with the Ultrafast Systems Surface Explorer Pro software.[4]

Nanosecond transient absorption measurements were performed with an Applied Photophysics laser flash photolysis apparatus, using a frequency-tripled (355 nm, 160 mJ) Surelite Continuum II Nd/YAG laser pulse (half-width 6-8 ns) as excitation source and a 150 W Xenon arc-lamp as probe light. Transient detection was obtained using a photomultiplier-oscilloscope combination (Hamamatsu R928, LeCroy 9360).

Electrochemical measurements were carried out in argon purged 1,2-dichloroethane at room temperature with an Autolab multipurpose equipment interfaced to a PC. The working electrode was a glassy carbon (8 mm^2, Amel) electrode. The counter electrode was a Pt wire, and the reference electrode was an SCE separated with a fine glass frit. The concentration of the complexes was about 5×10^{-4} M. Tetrabutylammonium hexafluorophosphate was used as a supporting electrolyte and its concentration was 0.05 M. Differential pulse voltammetry (DPV) was obtained at scan rates of 4, 10, 20 mV s^{-1}. Redox potentials were corrected by the internal reference ferrocene (395 mV vs. SCE).

UV−vis−NIR spectroelectrochemical measurements were obtained with a SPECAC Omni Cell System: an optically transparent thin-layer electrode (OTTLE) cell with the working Pt-mesh, twinned Ag-wire reference and Pt-mesh auxiliary electrodes melt-sealed into a polyethylene spacer – CaF$_2$ windows and 0.25 mm path length. The UV−vis−NIR spectra were registered with a JASCO V570 spectrophotometer concurrently applying a potential by using an Autolab multipurpose equipment interfaced to a PC. TBAPF$_6$, (+99%) supporting electrolyte and toluene solvent (anhydrous, 99.8%) were supplied by Aldrich.

Experimental uncertainties are as follows: absorption maxima, 2 nm; molar absorption, 15%; luminescence maxima, 4 nm; luminescence lifetimes, 10%; luminescence quantum yields, 15%; transient absorption decay and rise rates, 10%; redox potentials, 15 mV.

Förster rate constant for energy transfer process

Assuming Förster energy transfer as the leading mechanism, the rate constant can be calculated by the simplified equation S1.

$$k_{en}^{F} = 8.8x10^{-25} \frac{K^2\Phi}{n^4 r_{AB}^6 \tau} J_F$$

(S1)

In this equation, k_{en}^{F} is the rate constant of the energy transfer process, K is an orientation factor which accounts for the directional nature of the dipole-dipole interaction, Φ and τ are the luminescence quantum yield and lifetime of the donor model, respectively, n is the solvent refractive index, r_{AB} is the distance (in Å) between donor and acceptor. Considering the subunits of the species as freely rotating along the bond axis, the random value for the orientation factor (0.667) was assumed.

The overlap integral J_F for Förster interaction can be calculated according to equation S2.

$$J_F = \frac{\int F(\bar{v})\varepsilon(\bar{v})/\bar{v}^4 d\bar{v}}{\int F(\bar{v})d\bar{v}}$$

(S2)

In this equation, $F(\bar{v})$ is the luminescence spectrum of the donor model, and $\varepsilon(\bar{v})$ is the absorption spectrum of the acceptor on an energy scale (cm^{-1}).

This equation has been applied to calculate the energy transfer from the dirhenium chromophore to the fullerene subunit in **1**. The relevant spectroscopic and photophysical data were derived from the model species **2** and **3**. The orientation factor was assumed to be 2/3, the statistical value allowing free rotation. The donor-acceptor distance was assumed to be 10 Å, a quite, probably extreme, compact conformation (note that the dimension of the steroid moiety is 11 Å). With such approximations, time constant for the dirhenium-to-fullerene energy transfer according to the Förster mechanism in **1** is 13 ns, much slower than the experimental value of the quenching of dirhenium-based MMLCT excited state (about 100 ps, see main text).

Synthesis
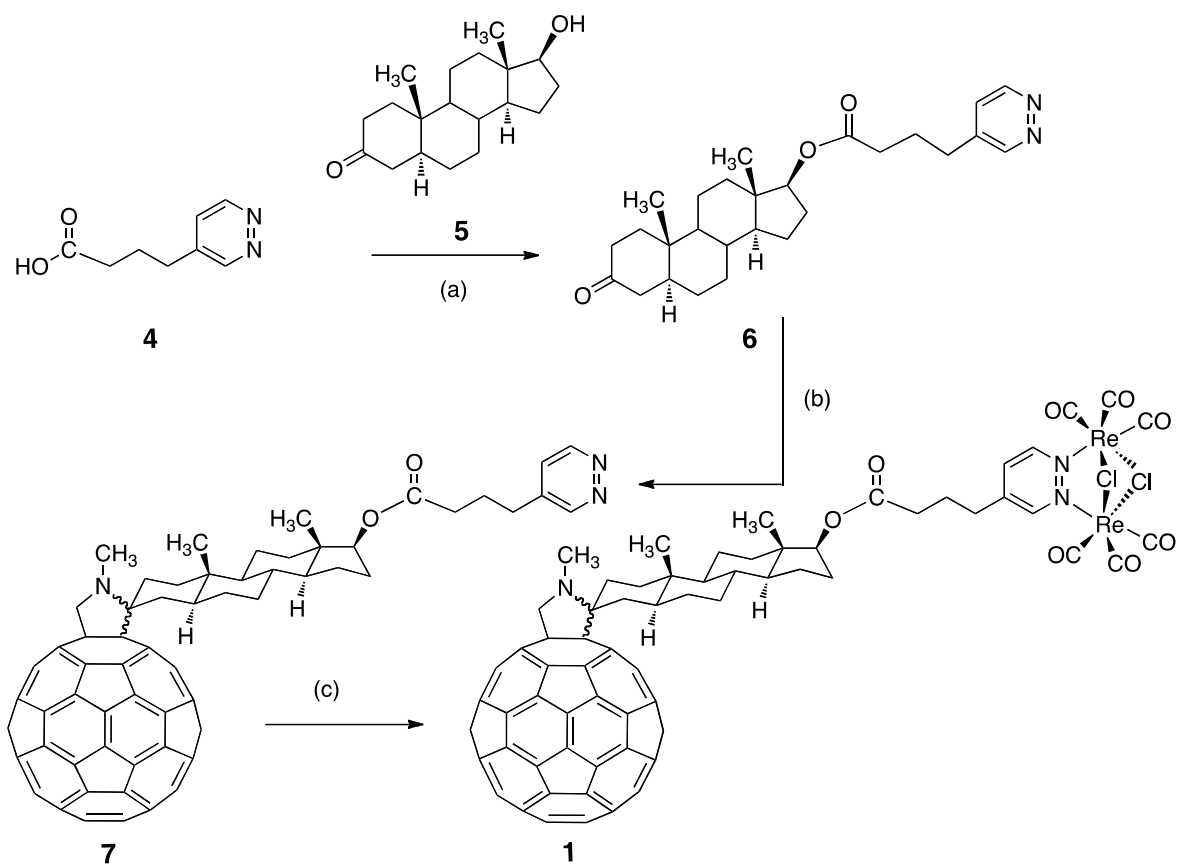
Scheme S1. Synthesis of dyad **1**. Reagents and conditions : (a) DCC/DMAP, CH$_2$Cl$_2$, 24h, 38%; (b) N- methylglycine, C$_{60}$, toluene, reflux, 4h, 10%; (c) [ReCl(CO)$_5$], toluene, reflux, 3 h, 70 %

Synthesis of ligand 6. N,N'-dicyclohexylcarbodiimide (DCC) (69 mg, 0.36 mmol), 4-(dimethylamino)pyridine (DMAP) (66 mg, 0.54 mmol) and 5α-androstan-17β-ol-3-one (84 mg, 0.29 mmol) were added in this order to a solution of 4-(pyridazine-4-yl)butanoic acid **4** (40 mg, 0.24 mmol) in CH$_2$Cl$_2$ (5 mL). The mixture was stirred at room temperature for 24 h, then water was added, the layers were separated and the organic phase was washed with NaHCO$_3$ 5% (3×15 mL), brine (3×15mL) and dried over Na$_2$SO$_4$. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (silica gel, toluene/AcOEt 6:4) affording 40 mg (38%) of **6** as a yellowish solid.

^{1}H NMR (300 MHz, CDCl$_3$) δ: 9.01 (m, 2H), 7.27 (m, 1H), 4.54 (t, 1H, J = 7.2 Hz), 2.63 (t, 2H, J = 7.5 Hz), 2.35-0.67 (m, 23H), 2.30 (t, 2H, J = 7.2 Hz), 2.03-1.80 (m, 2H), 0.95 (s, 3H), 0.73 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 211.7, 172.52, 152.60, 150.96, 140.62, 125.80, 82.85, 53.57, 50.41, 46.48, 44.51, 42.58, 38.36, 37.98, 36.78, 35.59, 35.03, 33.12, 31.64, 31.07, 28.61, 27.46, 24.71, 23.40, 20.78, 11.13, 11.35 ppm. ESI-MS (CH$_3$CN+0.1% HCOOH) m/z: [M+H]$^+$calcd. for

$(C_{27}H_{39}N_2O_3^+)$ 438.6; found 439.5 [M+H]. IR (KBr) ν: 3429, 3046, 2972, 2933, 2850, 1721, 1444, 1388, 1369, 1358, 1331, 1297, 1172, 1142, 1048, 1007, 979, 956, 879, 764, 730, 701 cm^{-1}.

Synthesis of fullerene ligand 7. Compound **6** (40 mg, 0.1 mmol) was added to a solution of [60]fullerene (55 mg, 0.08 mmol) and N-methylglycine (81 mg, 0.8 mmol) in toluene (56 mL). The mixture was heated to reflux temperature until complete consumption of **6** (TLC, toluene/AcOEt 6:4). The mixture was then cooled to room temperature, evaporated to dryness and the residue was purified by flash chromatography (silica gel, toluene/AcOEt 9:1, then 6:4). The resulting solid was dissolved in the minimum amount of toluene, precipitated from methanol and centrifuged, affording 11 mg (10%) of ligand **7** as a brown solid.

^{1}H NMR (250 MHz, CS$_2$/CDCl$_3$ 9:1) δ: 9.13-9.00 (m, 2H), 7.32-7.27 (m, 1H), 5.14-4.93 (m, 2H), 4.73-4.59 (m, 1H), 3.52 (s, 3H), 2.96 (s), 2.78-0.62 (m, 34H) ppm. ^{13}C NMR (63 MHz, CS$_2$/CDCl$_3$ 9:1) δ: 180.67, 163.26, 163.17, 161.01, 159.38, 155.29, 155.16, 154.93, 154.78, 154.70, 154.51, 154.47, , 154.45, 154.31, 154.29, 154.27, 153.89, 153.75, 153.71, 153.68, 153.62, 153.59, 153.56, 153.45, 152.97, 152.89, 152.85, 152.83, 151.72, 151.18, 151.13, 151.11, 151.09, 151.08, 150.80, 150.80, 150.71, 150.67, 150.66, 150.60, 150.41, 150.38, 150.34, 150.29, 150.25, 150.00, 148.91, 148.77, 148.72, 148.44, 148.38, 143.89, 143.82, 134.06, 92.36, 91.56, 88.36, 87.07, 84.65, 80.54, 77.91, 63.11, 63.06, 59.50, 51.77, 51.34, 51.15, 47.31, 45.79, 44.98, 44.37, 44.22, 43.93, 41.92, 41.86, 40.47, 40.43, 37.42, 36.34, 33.70, 32.29, 29.34, 20.97, 20.94, 9.55 ppm. APPI-MS (negative mode, cyclohexane) *m/z*: calcd. for C$_{89}$H$_{43}$N$_3$O$_2$ 1185, found 1185, 720 (C$_{60}$). UV-Vis (cyclohexane) λ: 431.5, 417.5, 318.5, 256.0, 231.0 nm.

Synthesis of the dyad 1. To a solution of [ReCl(CO)$_5$] (3.5 mg, 9.67 μmol) in freshly distilled toluene (4 ml) in a Schlenk tube, fullerene ligand **7** (5.6 mg, 4.73 μmol) was added and the mixture was refluxed for 3 h. The progress of the reaction was monitored by IR spectroscopy, following the disappearance of ν$_{CO}$ of [ReCl(CO)$_5$] at 2046 (s), 1985 (m) cm^{-1}. The solution was evaporated to dryness under reduced pressure and the residue, dissolved in CH$_2$Cl$_2$, was precipitated with *n*-hexane affording a microcrystalline powder that was purified by column chromatography (SiO$_2$, CH$_2$Cl$_2$). Dyad **1** (6.0 mg, 70%) was isolated upon addition of *n*-hexane to a concentrated CH$_2$Cl$_2$ solution as a brownish microcrystalline powder. Anal. Calcd for Re$_2$C$_{95}$H$_{43}$O$_8$N$_2$Cl$_2$: C, 63.47; H, 2.41; N, 2.34. Found: C, 63.71; H, 2.57; N, 2.28. IR (CH$_2$Cl$_2$) ν$_{CO}$: 2050 (mw), 2033 (s), 1947 (s), 1917 (s), cm^{-1}. These IR signals are characteristics of dinuclear Re complexes having idealized C$_{2v}$ symmetry and containing bridging nitrogen ligands and chlorides as ancillary ligands.[1c] ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ: 1.9-0.8 (m, 28H) 2.15 (q, 2H, H$_b$); 2.53 (t, 2H, H$_c$); 3.01 (t, 2H, H$_a$); 4.75 (t, 1H), 7.91-7.93 (dd, 1H, H$_5$); 9.64-9.69 (m, 2H, H$_3$, H$_6$). The insolubility of dyad **1** hampered the

registration of a meaningful ^{13}C NMR spectrum. UV-Vis (toluene) λ: 325, 435 nm.

Comments on the possible presence of diastereoisomers in 1

The use of a diastereoisomeric mixture of ligand **7** to bind Re(I) (see **Scheme S1**) may, in principle, influence properties such as the rates of energy or electron transfer, because diastereoisomers have different spatial orientations. In addition, the short alkyl chain that connects the androstane spacer to the pyridazine ligand moiety can generate a number of different conformations for each diastereoisomer that further complicate the assessment of the respective orientation of the donor and acceptor moieties in dyad **1**. One of us considered these structural issues in a previous paper (cited in reference no. 17 of the main paper, i.e.: M. Maggini, *et al.*, *Chem. Eur. J.*, 1998, **4**, 1992-2000), whose topic is closely related to that of the present work, and found that diastereoisomerically pure dyads, based on the same androstane spacer as dyad **1**, essentially behave like their diastereoisomeric mixture when separately tested in photophysical experiments. Therefore, whereas diastereoisomers mixture can be present in **1**, this circumstance is not important for the photophysical properties here studied. The situation resembles the negligible effect of the presence of chiral isomers for photoinduced electron and energy transfer processes involving multimetallic compounds based on octahedral Ru(II)-polypyridine compounds.[5]
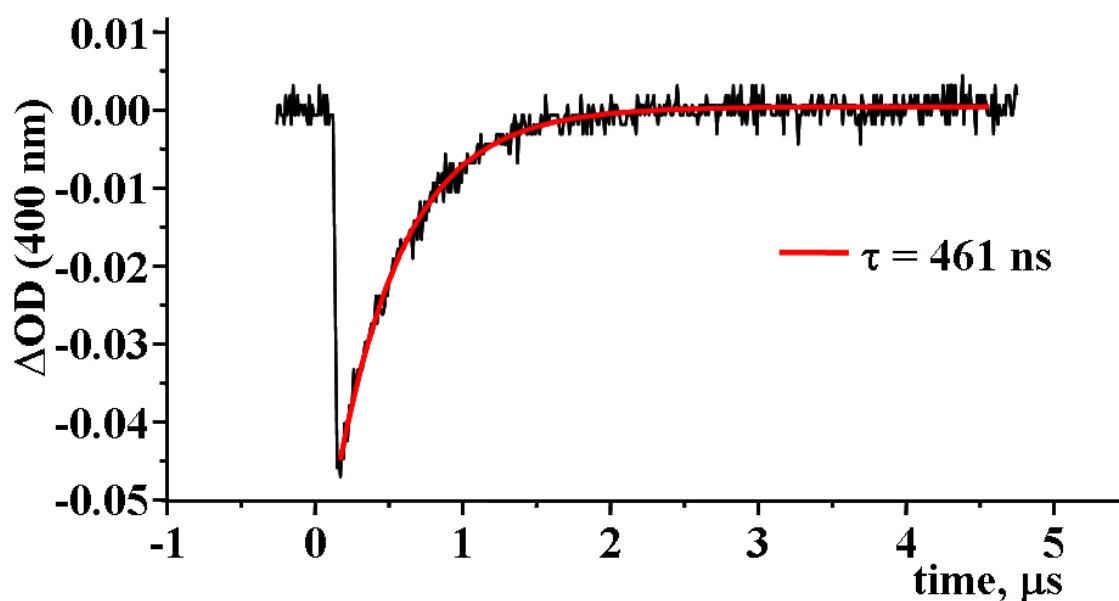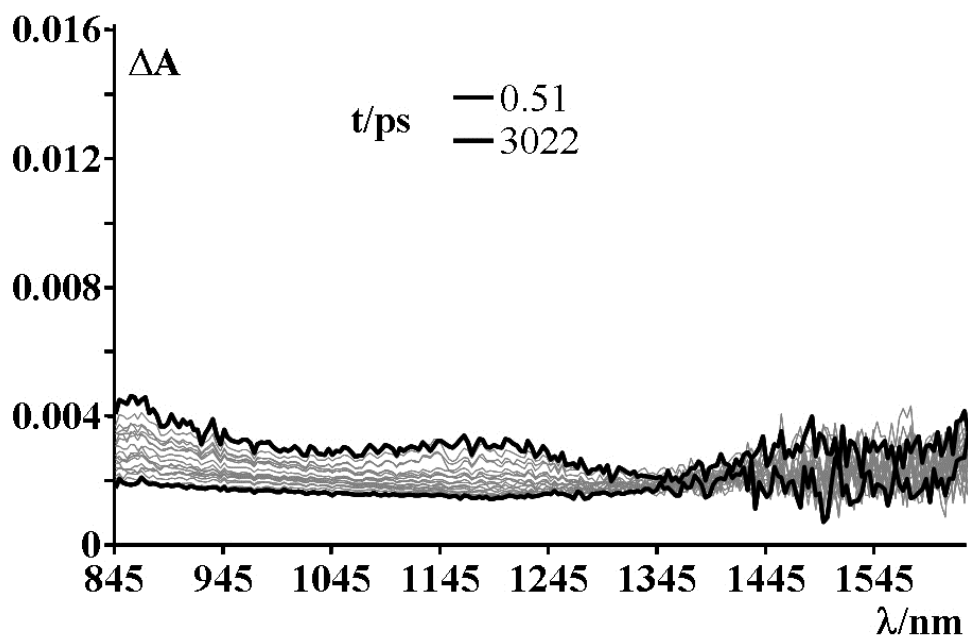
**Figure S1.** Time-dependent recovery of the MLLCT bleaching at 400 nm of **2** upon 355 nm excitation.
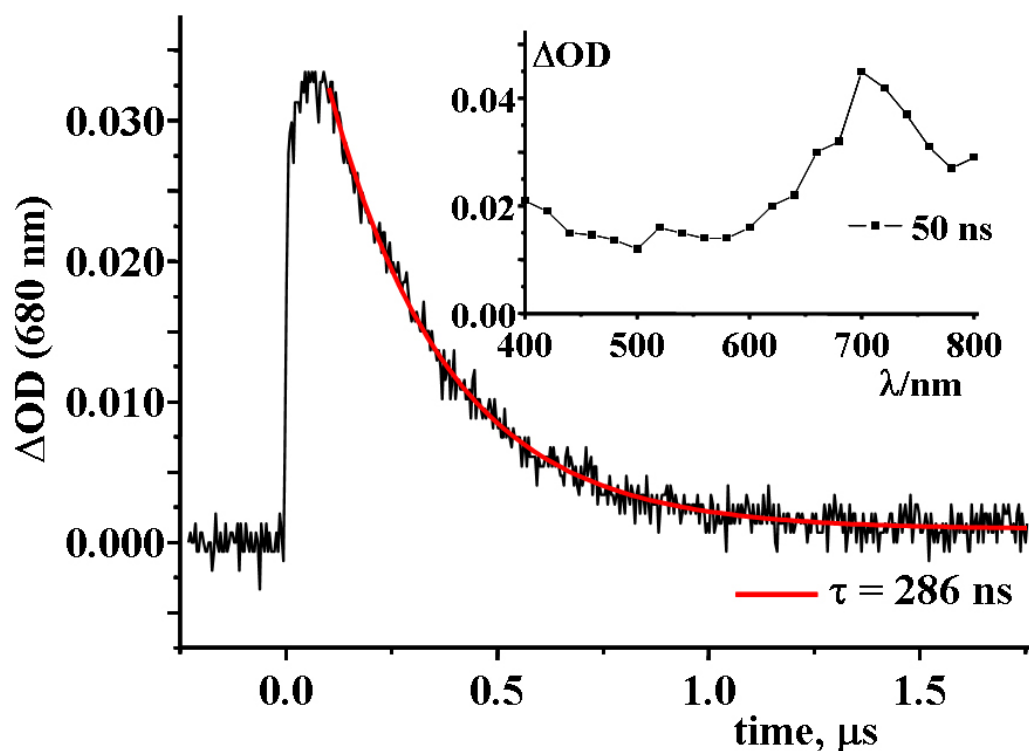
Figure S2. Transient absorption decay of **1** at 680 nm upon 355 nm excitation. For short delays after laser pulse a risetime is evidenced, which anyway is too fast to be calculated (<10 ns). In the inset, the transient absorption spectrum of **1** after 50 ns from pulse is shown.
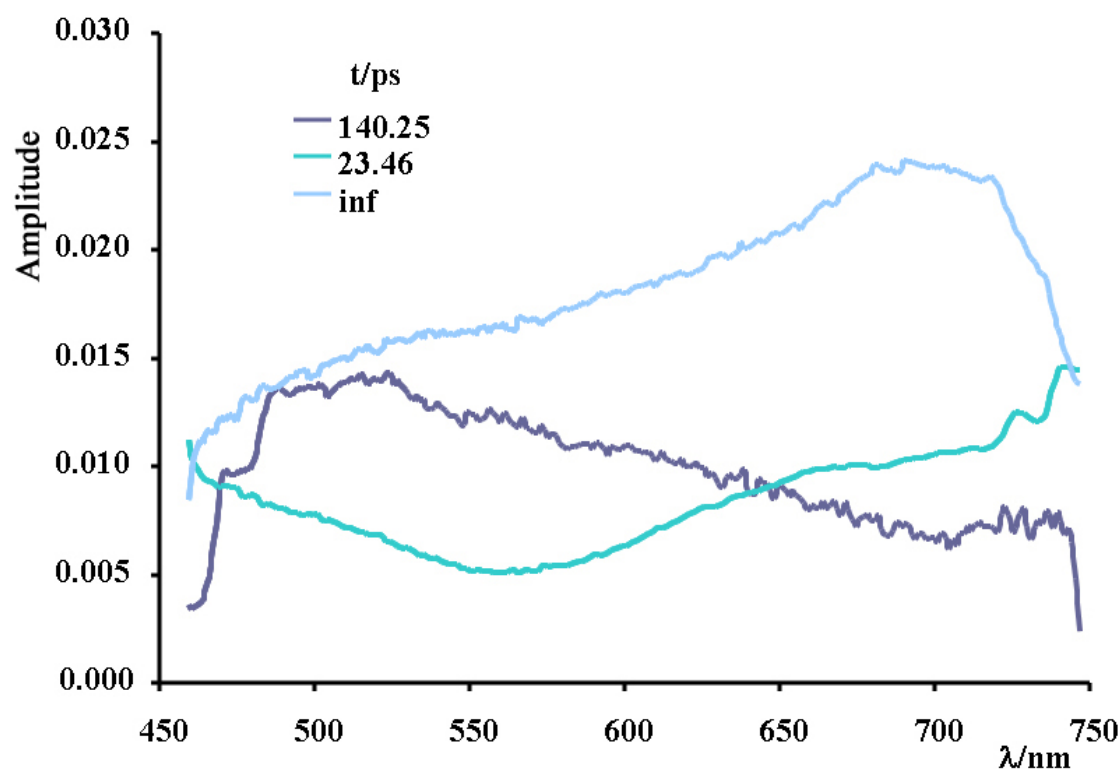
Figure S3. NIR transient spectra of **2**. No significant spectral feature is apparent.
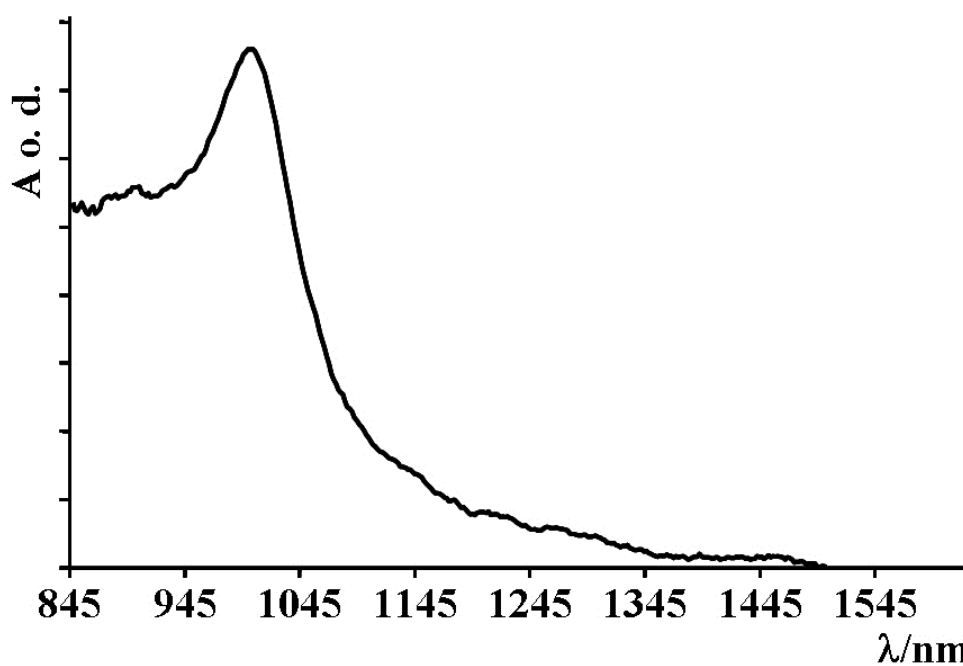
Figure S4. Spectroelectrochemistry of **3**. The spectrum is obtained by applying a potential of -0.85 V vs SCE at a solution of **3** in toluene. The peak maximum corresponds to the peak obtained in the spectra of Figure 6, top panel, attributed to the CS state.

Figure S5. Spectral distributions of the pre-exponential amplitudes of the three lifetime components obtained for **1,** via global analysis on the singular value decomposition (SVD) of the principal spectral components of the transient absorption spectra. Comments in the text reported in ESI.

Comments on the global kinetic analysis of 1

A global kinetic analysis was performed on the transient absorption spectra of **1** (see **Figure S5**). The analysis yields three reliable components. The shortest one (τ about 23 ps), which is similar to the initial transient spectrum shown in **Figure 5a**, fits the global time for vibrational cooling within the MLLCT triplet state of the metal center (two processes are calculated by single wavelength analysis for vibrational cooling, see **Figs. 5** and **6** in the main text, with 4 and 20 ps time constants; the shorter-lived process is not evidenced by global analysis); the second component (τ about 140 ps) agrees with the transient spectrum shown in **Figure 5b**, and is assigned to the charge-separated state (which is actually calculated to decay with a time constant of about 120 ps, see main text); the final spectrum, which has a decay time constant longer than the pump-probe experiment limit (3 ns), recalls the final spectrum in **Figure 5c**, and is assigned to the triplet state of the fullerene subunit (which indeed decays in the ns-μs regime, see main text and **Figure S2**).

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