SUPPLEMENTARY INFORMATION

Extremely fast triplet formation by charge recombination in a Nile Red/fullerene flexible dyad

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1. <u>Synthesis</u>

General methods

Dry solvents were prepared according to standard procedures, distilled before use and stored over 3 or 4 Å molecular sieves. Most of the solvents and reagents were obtained from commercial sources and used without further purification. Analytical TLC was performed using prepared plates of silica gel (Merck 60 F-254 on aluminum). Merck silica gel 60 (70-230 mesh) was used for flash chromatography and for preparative TLC plates. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 300 or AV400 spectrometer. All chemical shifts are reported in part per million (ppm) using the residual peak of the deuterated solvent, whose values are referred to tetramethylsilane (TMS, δ_{TMS}= 0), as internal standard. All ^{13}C NMR spectra were performed with proton decoupling. Mass spectra were recorded in ESI mode on a single quadrupole instrument SQ Detector, Waters (capillary voltage 3.7 kV, cone voltage 30-160 eV, extractor voltage 3 eV, source block temperature 80 °C, desolvation temperature 150 °C, cone and desolvation gas (N$_2$) flow rates 1.6 and 8 L/min, respectively).

5-Hydroxycarbonyl-25,26,27,28-tetrapropoxycalix[4]arene **7** was synthesized according to a literature procedure.[1]

Synthesis of C$_{60}$-calix[4]arene (5):

C$_{60}$-calix[4]arene **5** was synthesized from calix[4]arene **7** according to the following pathway:
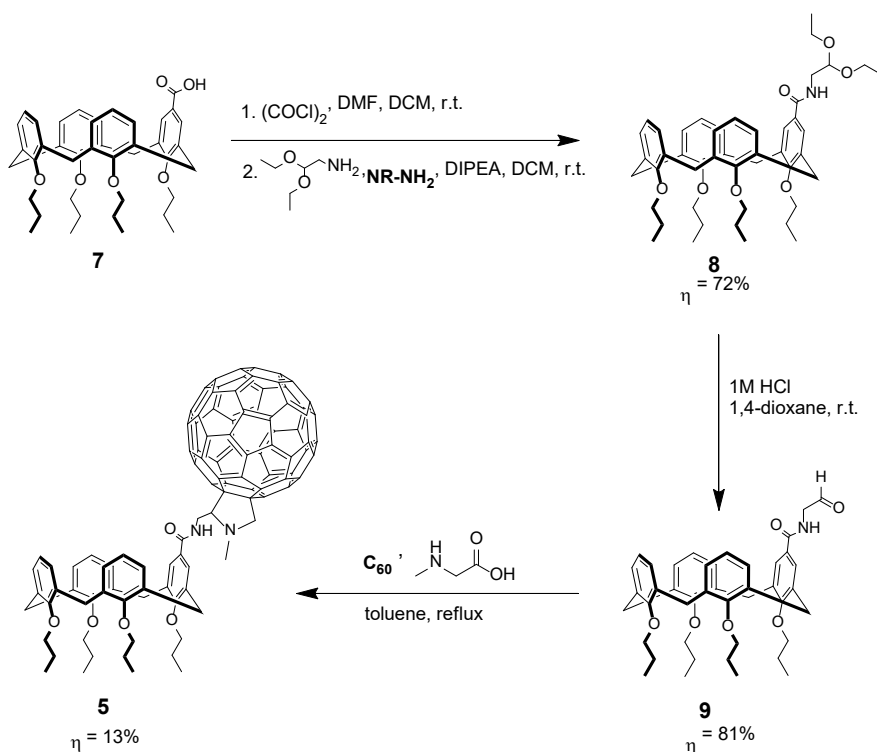
5-(2,2-diethoxyethyl)carbamoyl-25,26,27,28-tetrapropoxycalix[4]arene (8):

To a solution of **7** (187 mg, 0.29 mmol) in dry DCM (30 mL), oxalyl chloride (385 µL, 4.41 mmol) was added, together with few drops of dry DMF. The mixture was stirred for 3 hours at room temperature under nitrogen atmosphere and the solvent removed at reduced pressure. The acyl chloride thus obtained was redissolved in dry DCM (25 mL) and 2,2-diethoxyethanamine (64 µL, 0.44 mmol) and DIPEA (0.31 mL, 1.76 mmol) were added. The mixture was allowed to stir overnight under nitrogen. The reaction was quenched with 1M HCl (30 mL) and the organic layer separated. The aqueous phase was extracted with DCM and the organic layers were reunited, washed twice with water and concentrated under pressure. The residue was purified by column chromatography (hexane/AcOEt 8:2) to give the desired compound in 72% yield (158 mg, 0.21 mmol). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 6.89 (s, 2H, ArHCO), 6.79 (d, J = 7.4 Hz, 4H, ArH), 6.70 (t, J = 7.2 Hz, 2H, ArH), 6.44 (s, 3H, ArH), 5.86 (t, J = 5.8 Hz, 1H, NH), 4.57 (t, J = 5.4 Hz, 1H, CH(OCH$_2$CH$_3$)$_2$), 4.50 (d, J = 13.5 Hz, 2H, ArCHH$_{ax}$Ar) 4.48 (d, J = 13.5 Hz, 2H, ArCHH$_{ax}$Ar), 4.01-3.79 (m, 8H, OCH$_2$), 3.79-3.69 (m, 2H, OCHHCH$_3$), 3.64-3.55 (m, 2H, OCHHCH$_3$), 3.51 (t, J = 5.6 Hz, 2H, NHCH_2), 3.21 (d, J = 13.5 Hz, 2H, ArCHH$_{eq}$Ar), 318 (d, J = 13.5 Hz, 2H, ArCHH$_{eq}$Ar), 2.01-1.86 (m, 8H, OCH$_2$CH_2), 1.28 (t, J = 7.1 Hz, 6H, OCH$_2$CH_3), 1.06 (t, J = 7.4, Hz, 6H, OCH$_2$CH$_2$CH_3), 1.00 (t, J = 7.5 Hz, 6H, OCH$_2$CH$_2$CH_3). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 167.6, 159.2, 156.9, 156.2, 135.8, 135.1, 135.0, 134.6, 128.6, 128.4, 128.0, 127.7, 126.7, 122.1, 121.8, 100.9, 62.9, 42.3, 31.05, 31.02, 23.3, 23.1, 15.4, 10.5, 10.4, 10.1. ESI-MS: m/z calcd for C$_{47}$H$_{61}$NO$_7$Na [(**8**+Na)$^+$] 774.4, found 774.5 (100%); calcd for C$_{47}$H$_{61}$NO$_7$K [(**8**+K)$^+$] 790.5, found 790.5 (20%).

5-(2-oxoethyl)carbamoyl-25,26,27,28-tetrapropoxycalix[4]arene (9):

After dissolving compound **8** (15 mg, 0.21 mmol) in 1,4-dioxane (30 mL), 1M HCl (20 mL) was added and the mixture allowed to stir at room temperature for 21 hours. After reaction completion the solvent was partly evaporated under reduced pressure, then DCM (30 mL) and H$_2$O (15 mL) were added to the flask and the two phases separated. The aqueous layer was extracted with DCM and the organic phases reunited and washed twice with water (2x60 mL) to neutral pH, then concentrated under reduced pressure. The residue was purified by column chromatography (Hexane/AcOEt 7:3) to afford the compound as a whitish solid (115 mg, 0.17 mmol, 81% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 9.74 (s, 1H, CHO), 6.98 (s, 2H, ArHCO), 6.75-6.63 (m, 6H, ArH), 6.53 (d, J = 7.5 Hz, 2H, ArH), 6.41 (t, J = 7.5 Hz, 1H, ArH), 6.36 (br s, 1H, NH), 4.49 (d, J = 13.5, 2H, ArCHH$_{ax}$Ar), 4.46 (d, J = 13.5, 2H, ArCHH$_{ax}$Ar), 4.31 (d, J = 4.7 Hz, 2H, NHCH_2), 3.93-3.78 (m, 8H, OCH$_2$), 3.21 (d, J = 13.5, 2H, ArCHH$_{eq}$Ar), 4.19 (d, J = 13.5, 2H, ArCHH$_{eq}$Ar), 1.98-1.87 (m, 8H, OCH$_2$CH_2), 1.07-0.95 (m, 12H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 196.5, 167.7, 159.8, 156.7, 156.4, 135.5, 134.9, 134.7, 128.6, 128.3, 127.9, 127.0, 122.2, 122.1, 121.7, 50.7, 31.04, 31.00, 23.33, 23.31, 23.2, 10.42, 10.40, 10.2. ESI-MS: m/z calcd for C$_{43}$H$_{51}$NO$_6$Na [(**9**+Na)$^+$] 700.4, found 701.0 (100%); calcd for C$_{43}$H$_{51}$NO$_6$K [(**9**+K)$^+$] 716.5, found 717.3 (40%).

C$_{60}$-calix[4]arene (5):

To a solution of **9** (120 mg, 0.18 mmol) in dry toluene (20 mL), N-methylglycine (32 mg, 0.25 mmol) and fullerene C$_{60}$ (128 mg, 0.18 mmol) were added and the mixture heated to reflux for 3 hours, after which the solvent was evaporated under vacuum. The residue was dissolved in DCM and washed twice with water, then the DCM was evaporated at reduced pressure. The solid was purified by preparative TLC plates (DCM) to give a brownish solid in 13% yield (32 mg, 0.022 mmol). Mp: > 300 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.02 (s, 2H, ArHCO), 6.81 (br s, 1H, NH), 6.70-6.46 (m, 9H, ArH), 4.98 (d, J = 9.5 Hz, 1H, CH$_3$NCHH), 4.81 (dd, J = 14.6, 6.9 Hz, 1H, NHCHH), 4.51-4.41 (m, 4H, ArCHH$_{ax}$Ar), 4.26 (d, J = 9.5 Hz, 1H, CH$_3$NCHH), 4.21 (br s, 1H, NHCH$_2$CH), 4.13 (d, J = 14.8 Hz, 1H, NHCHH), 3.91-3.80 (m, 8H, OCH$_2$), 3.22-3.14 (m, 4H, ArCHH$_{eq}$Ar), 3.01 (s, 3H, NCH$_3$),

1.97-1.86 (m, 8H, OCH$_2$CH_2), 1.06-0.94 (m, 12H, CH$_3$). ESI-MS: m/z calcd for C$_{105}$H$_{57}$N$_2$O$_5$ [(**5**+H)$^+$] 1425.4, found 1425.8.

Synthesis of reference compound C$_{60}$-Ph:

C$_{60}$-Ph was synthesized in one step from N-(2-Oxo-ethyl)benzamide according to the following scheme:
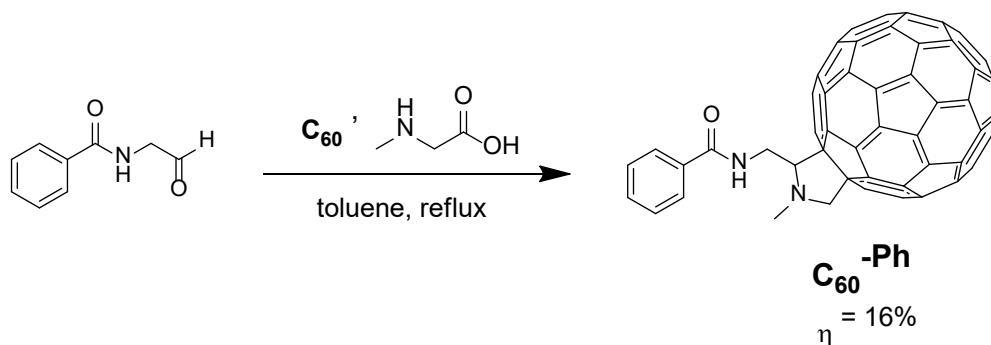
C$_{60}$-Ph:

To a solution of N-methylglycine (30 mg, 0.34 mmol) and fullerene C$_{60}$ (185 mg, 0.26 mmol) in dry toluene (20 mL), N-(2-Oxo-ethyl)benzamide (30 mg, 0.17 mmol) was added and the mixture heated to reflux for 2.5 hours, after which the solvent was evaporated under vacuum. The solid residue was purified by column chromatography (gradient toluene – toluene/ethyl acetate 7:3, v/v) to give a brownish solid in 16% yield (25 mg, 0.03 mmol). ^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.75 (bs, 2H, ArH), 7.50-7.41 (m, 3H, ArH), 7.20 (bs, 1H, NH), 4.95-4.82 (m, 2H, NHCHH and CH$_3$NCHH), 4.24 (bs, 3H, NHCHH, CH$_3$NCHH and CH$_3$NCHC), 3.01 (s, 3H, NCH$_3$). ESI-MS: m/z calcd for C$_{71}$H$_{15}$N$_2$O [(**C$_{60}$-Ph**+H)$^+$] 911.1, found 911.2.
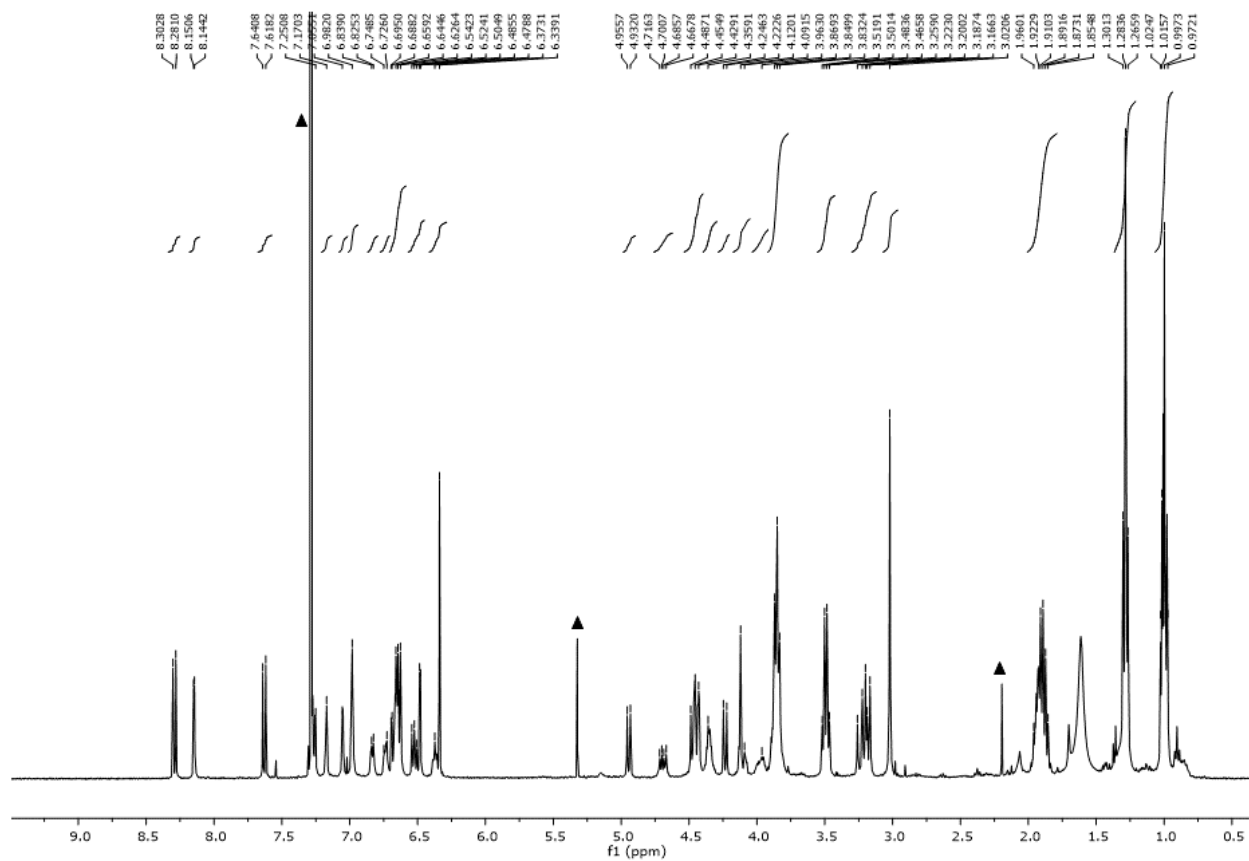
2. <u>¹H NMR Spectroscopy</u>

Fig. S1. ¹H NMR spectrum (400 MHz, CDCl₃) of compound **3**. ▲ indicates residual solvent impurities.
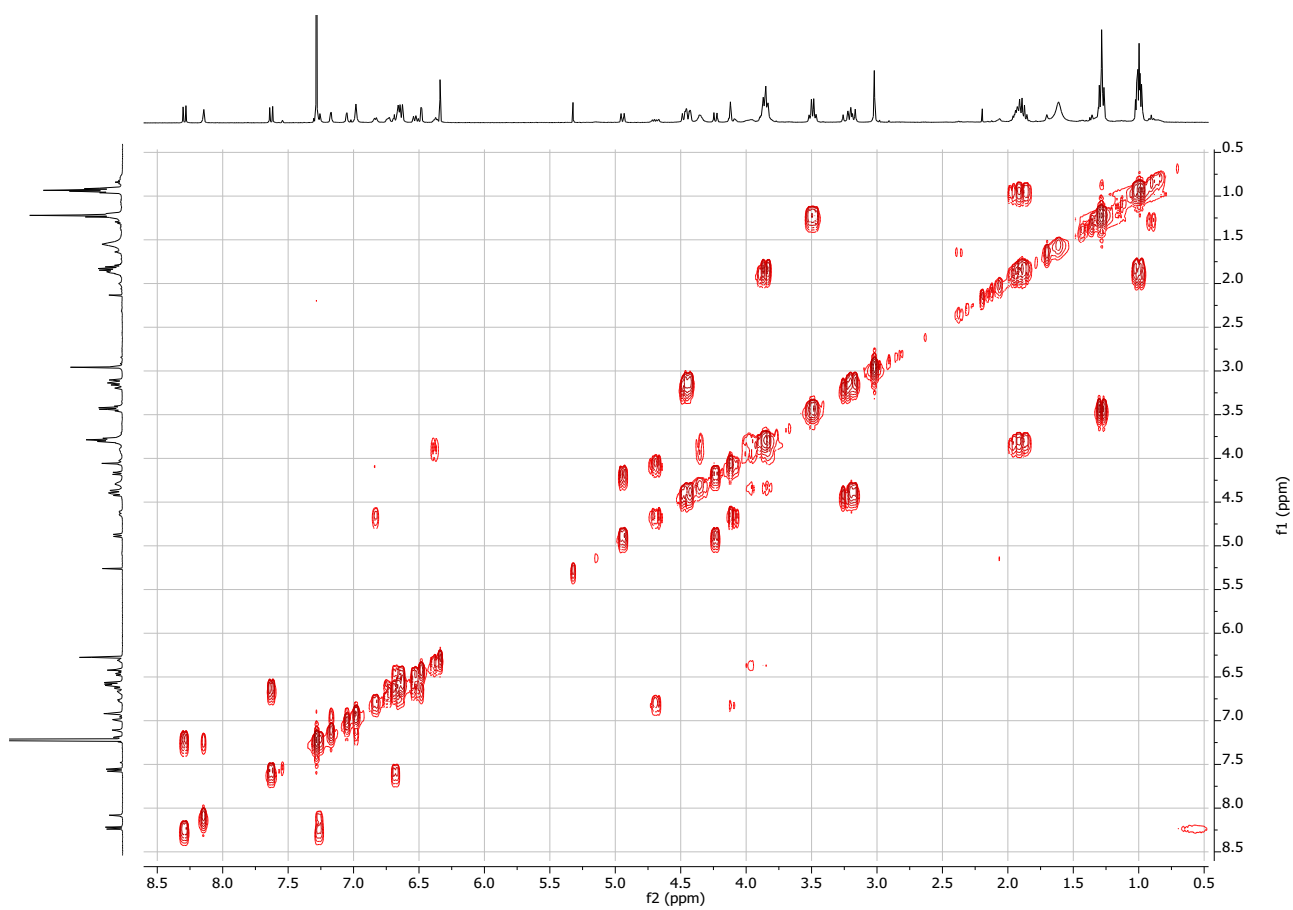
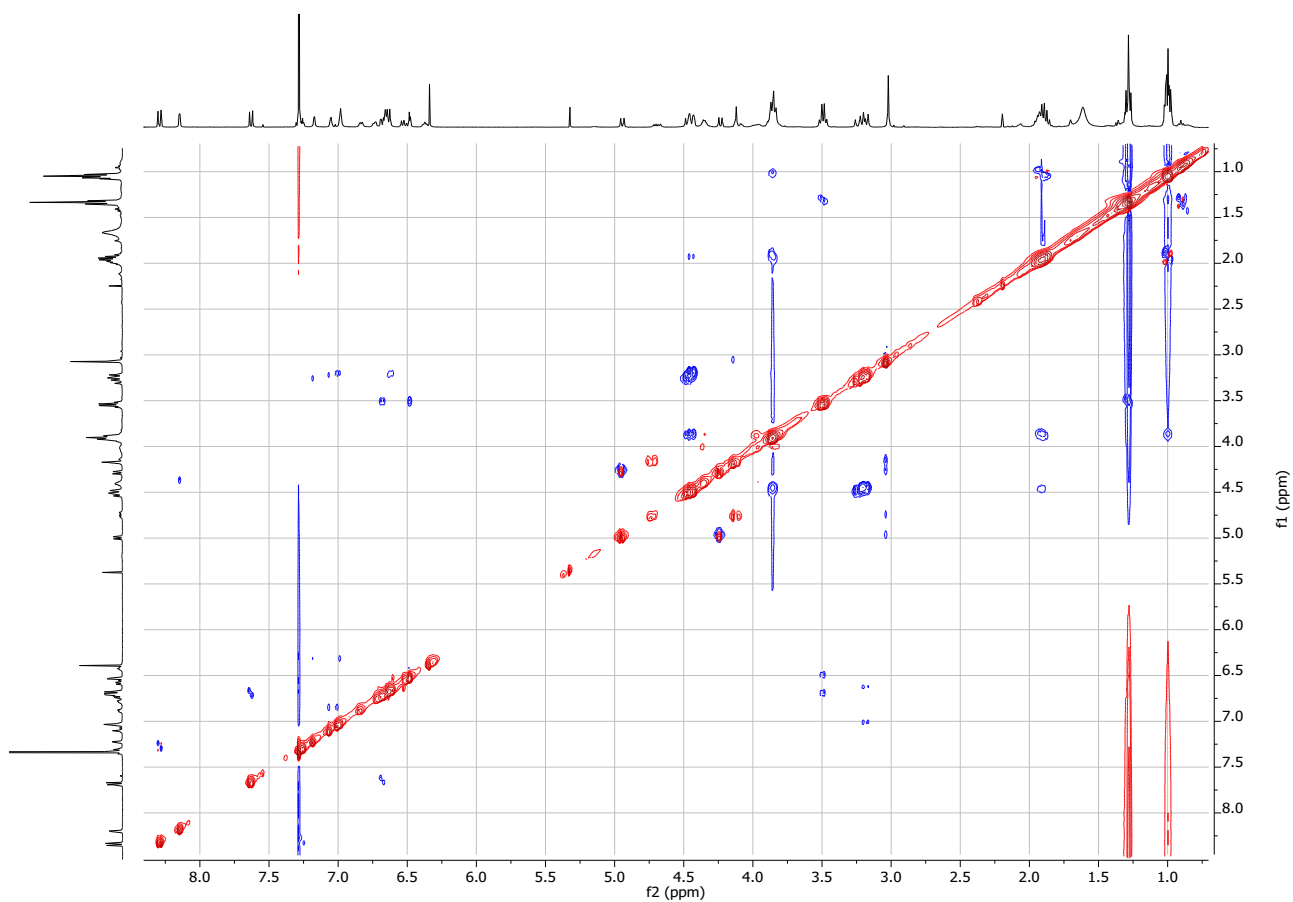**Fig. S2.** COSY spectrum (400 MHz, CDCl₃) of compound **3**.

Fig. S3. ROESY spectrum (400 MHz, CDCl₃) of compound **3**.

3. Computational results

open

open_C60
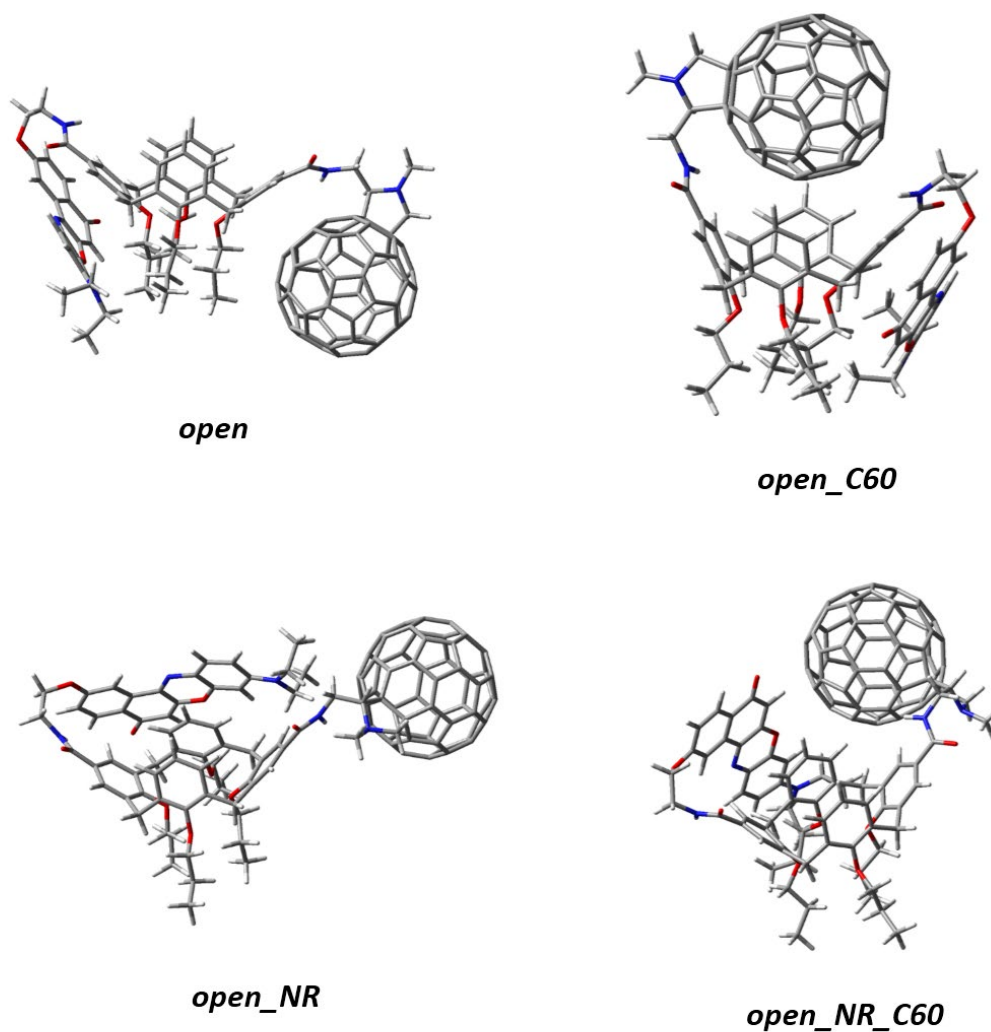
open_NR

open_NR_C60

Fig. S4. Selected conformers of the NR-calix-C60 dyad (geometry optimized in gas phase).

Table S1. Total free energy of the conformers optimized at ωB97XD/6-31G level in gas phase. The energy of the most stable conformer is set to zero. Center-to-center distance R_{CC} between Nile Red and C_{60} in the optimized structures.

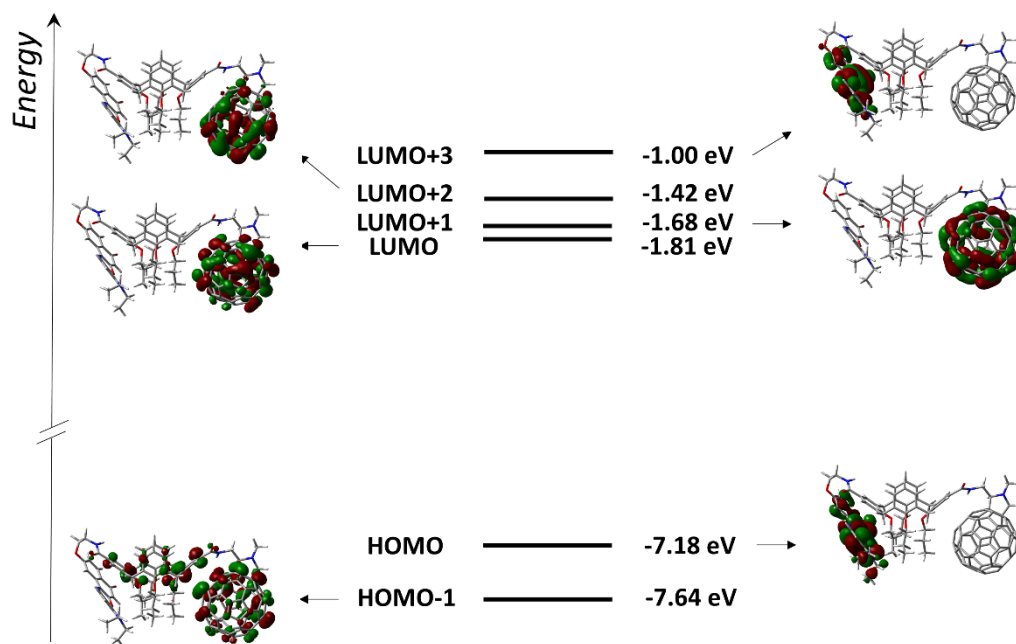|	Free energy (kcal mol^{-1})	R_{CC} (Å)	
	Gas phase	Gas phase	Toluene
open	0.00	14.019	14.067
open_NR	0.25	11.053	--
open_NR_C60	2.62	7.915	--
open_C60	4.13	10.739	--

Fig. S5. FMOs (isovalue 0.02) and corresponding energies of the *open* conformer in gas phase.
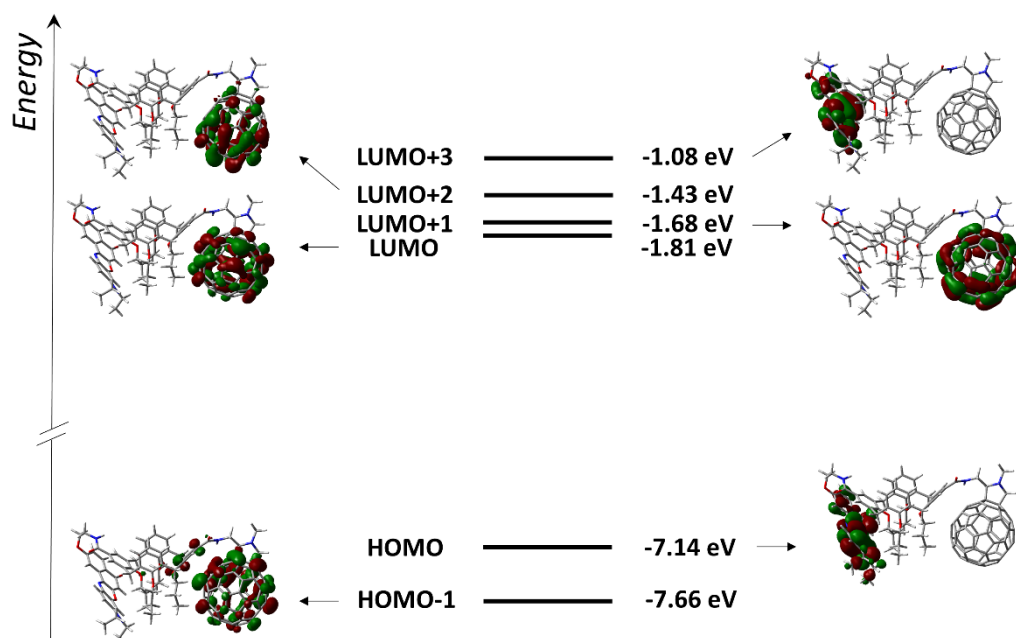

Fig. S6. FMOs (isovalue 0.02) and corresponding energies of the *open* conformer in toluene.
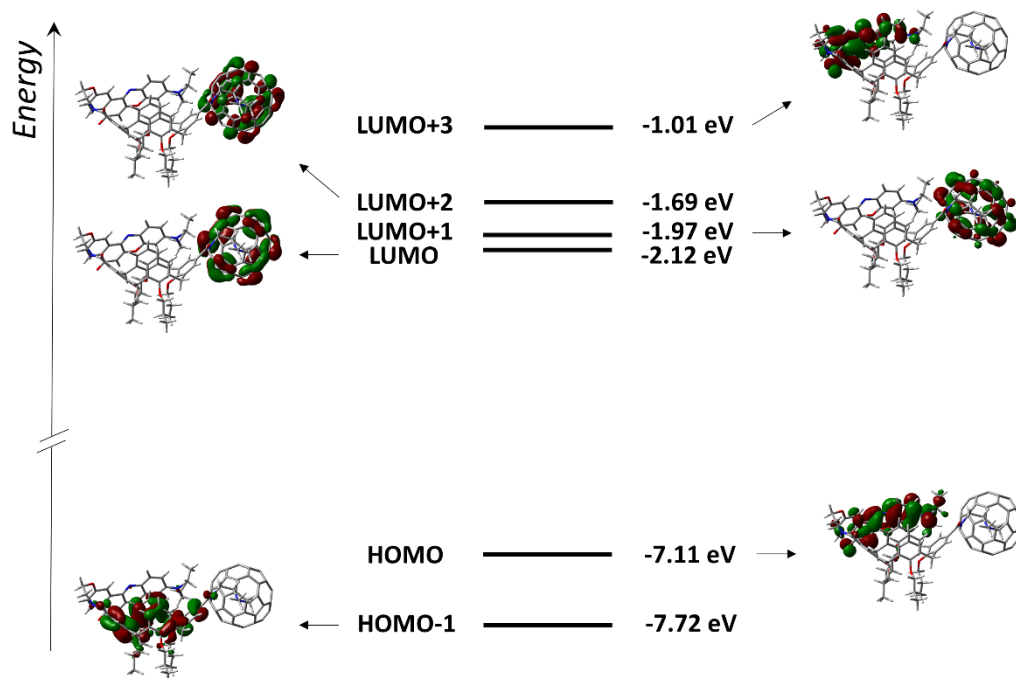
Fig. S7. FMOs (isovalue 0.02) and corresponding energies of the *open_NR* conformer in gas phase.
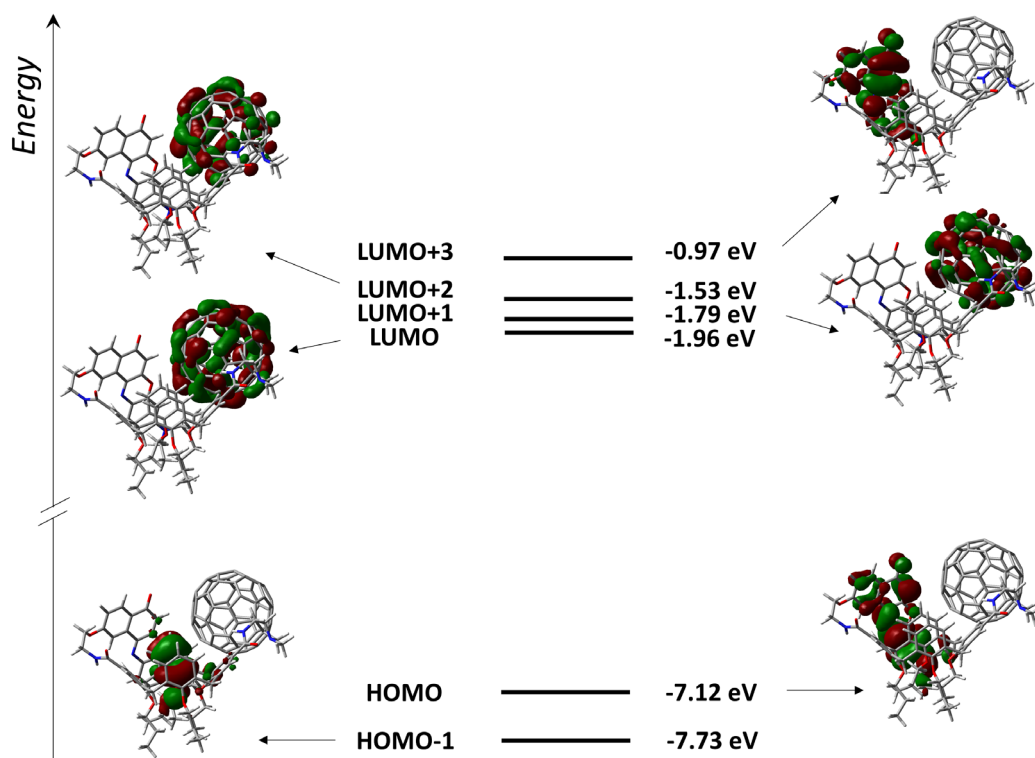

Fig. S8. FMOs (isovalue 0.02) and corresponding energies of the *open_NR_C60* conformer in gas phase.
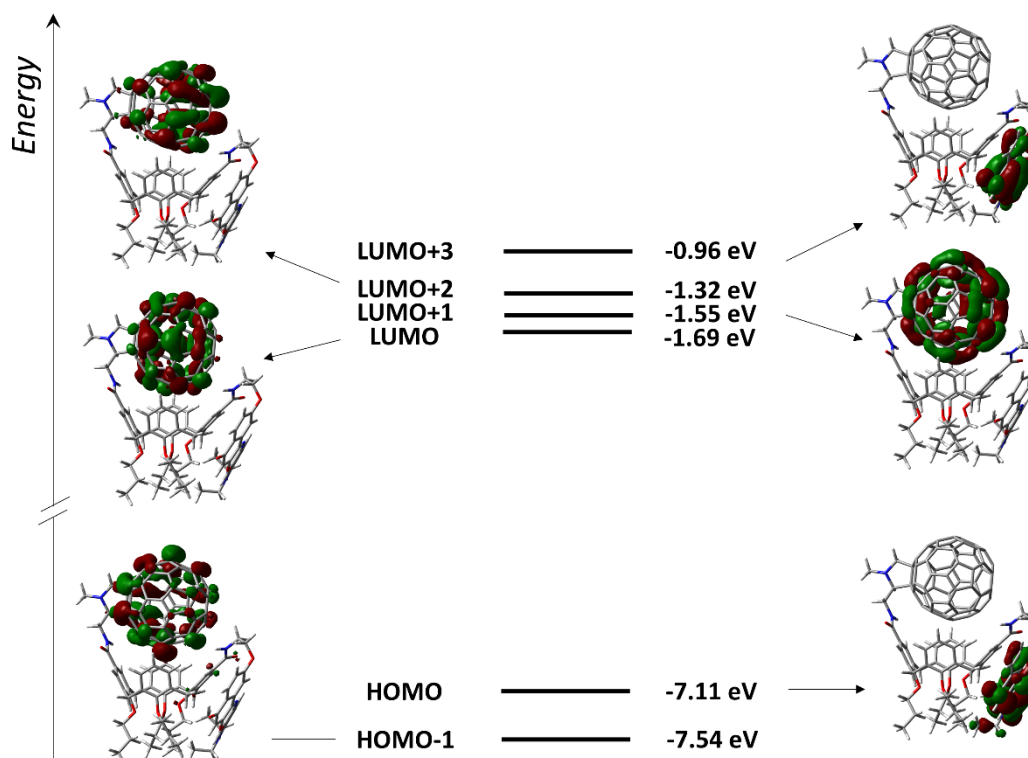
Fig. S9. FMOs (isovalue 0.02) and corresponding energies of the ***open_C60*** conformer in gas phase.

4. <u>Rehm-Weller analysis</u>

The Gibbs free energy change (ΔG_{CS}) of the charge-separation process was calculated using the Rehm-Weller equation:[2]

$$\Delta G_{CS} = e[E_{ox} - E_{red}] - E_{00} + \Delta G_s$$

where E_{ox} is the half-wave potential for one-electron oxidation of the electron-donor unit, and E_{red} is the half-wave potential for one-electron reduction of the electron-acceptor unit; E_{00} is the energy level approximated with the crossing point of the normalized UV-vis absorption and fluorescence emission spectra of the singlet excited state (LE state on Nile Red); ΔG_s is the static Coulombic energy, given by:

$$\Delta G_s = -\frac{e^2}{4\pi\varepsilon_0\varepsilon_s R_{CC}} - \frac{e^2}{8\pi\varepsilon_0}\left(\frac{1}{R_D} + \frac{1}{R_A}\right)\left(\frac{1}{\varepsilon_{REF}} - \frac{1}{\varepsilon_s}\right)$$

where ε_s is the static dielectric constant of the solvent, R_{CC} is the center-to-center D–A distance optimized by DFT calculations, R_D (R_A) is the radius of the electron donor (acceptor), ε_{REF} is the static dielectric constant of the solvent used for the electrochemical studies, and ε_0 is the vacuum permittivity.

The energy of the charge-separated state (E_{CS}, relative to the ground state) can be estimated as follows:

$$E_{CS} = e[E_{ox} - E_{red}] + \Delta G_s$$

Table S2. Charge separation free energy (ΔG_{CS}) and energy of the charge-separated state (E_{CS}) for the different conformers.

	ΔG_{CS} (eV) [a]	E_{CS} (eV) [a]
open	0.0834	2.34
open_NR	- 0.0339	2.22
open_NR_C60	- 0.2509	2.00
open_C60	- 0.0499	2.20

[a] Values obtained with the Rehm-Weller equation, using the redox potentials measured in dichloromethane (ε_{REF} = 8.93), R_D = 5.0 Å and R_A = 3.5 Å, R_{CC} as obtained by geometry optimization in gas phase, E_{00} = 2.25 eV (as experimentally determined in toluene), and ε_s = 2.38 (as relevant to toluene).

5. <u>Singlet oxygen generation</u>

Singlet oxygen quantum yields ϕ_Δ of compounds **3** and **5** in toluene and chloroform were estimated exploiting the near-IR luminescence of $^1O_2$ (peaked at $\lambda \approx 1270$ nm). Measurements were performed on air-equilibrated solutions.

Values of ϕ_Δ were estimated as follows:[3]

$$\phi_\Delta = \phi_{\Delta(R)} \frac{\alpha_R}{\alpha} \frac{I}{I_R} \frac{n^2}{n_R^2} \frac{\tau_{\Delta(R)}}{\tau_\Delta}$$

where $\phi_{\Delta(R)}$ is the quantum yield of the standard, n is the solvent refracctive index, τ_Δ is the phosphorescence lifetime of $^1O_2$, I is the emission intensity corrected for primary inner filter effect ($I = I_{exp} 10^{A/2}$, with I_{exp} the integral of the experimental emission spectrum and A the absorbance at the excitation wavelength), and $\alpha = 1 - 10^{-A}$. The subscript (R) refers to the reference standard.

Compound **5** in toluene was used as the standard, assuming $\phi_{\Delta(R)} = 1.0$.[4]

Values obtained with this method are reported in Table S3.

Table S3. Singlet oxygen generation of compounds **3** and **5** in toluene and chloroform: excitation wavelength (λ_{exc}), $^1O_2$ phosphorescence lifetime (τ_Δ), singlet oxygen quantum yield (ϕ_Δ). Compound **5** in toluene was used as reference ($\phi_\Delta = 1.00$).

Solvent	τ_Δ (µs)	Compound	λ_{exc} (nm)	ϕ_Δ
Toluene	29.53	**3**	530	1.07
		5	370	1.00
Chloroform	246.01	**3**	540	0.52
		5	370	0.53

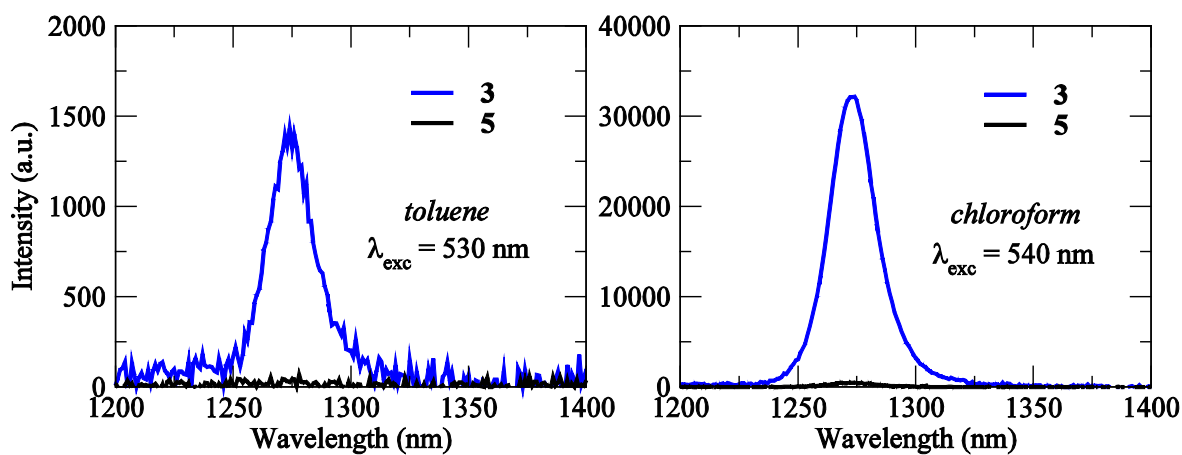**Fig. S10.** $^1O_2$ emission spectra obtained upon excitation of **3** and **5** in the visible, collected under the same experimental conditions ($c = 2 \times 10^{-5}$ M). The low intensity observed for **5** is related to the low molar extinction coefficient of C_{60} at the excitation wavelength.
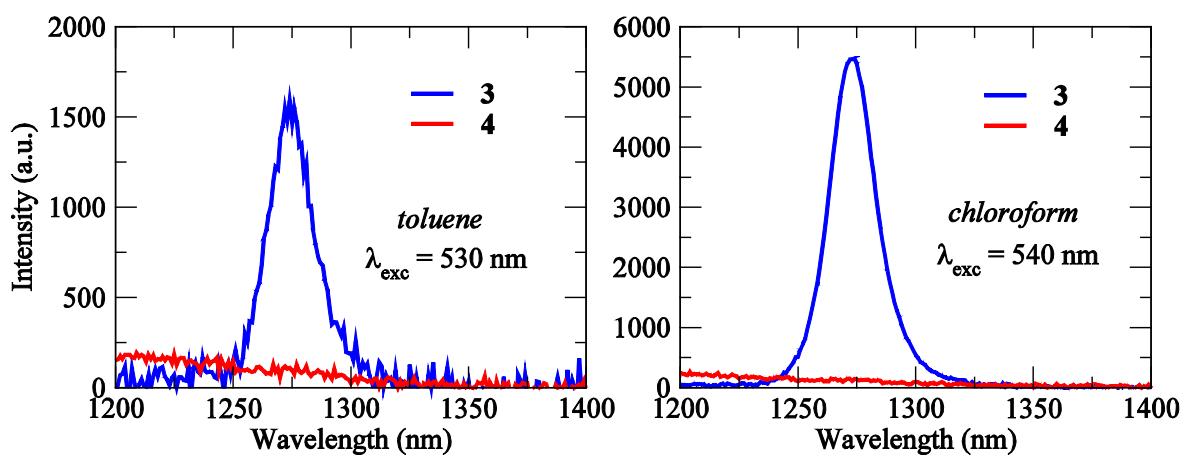

Fig. S11. $^1O_2$ emission spectra obtained for excitation of air-equilibrated solutions of compounds **3** and **4** in toluene and chloroform. Spectra were collected on iso-absorbing solutions at the excitation wavelength λ_{exc}.
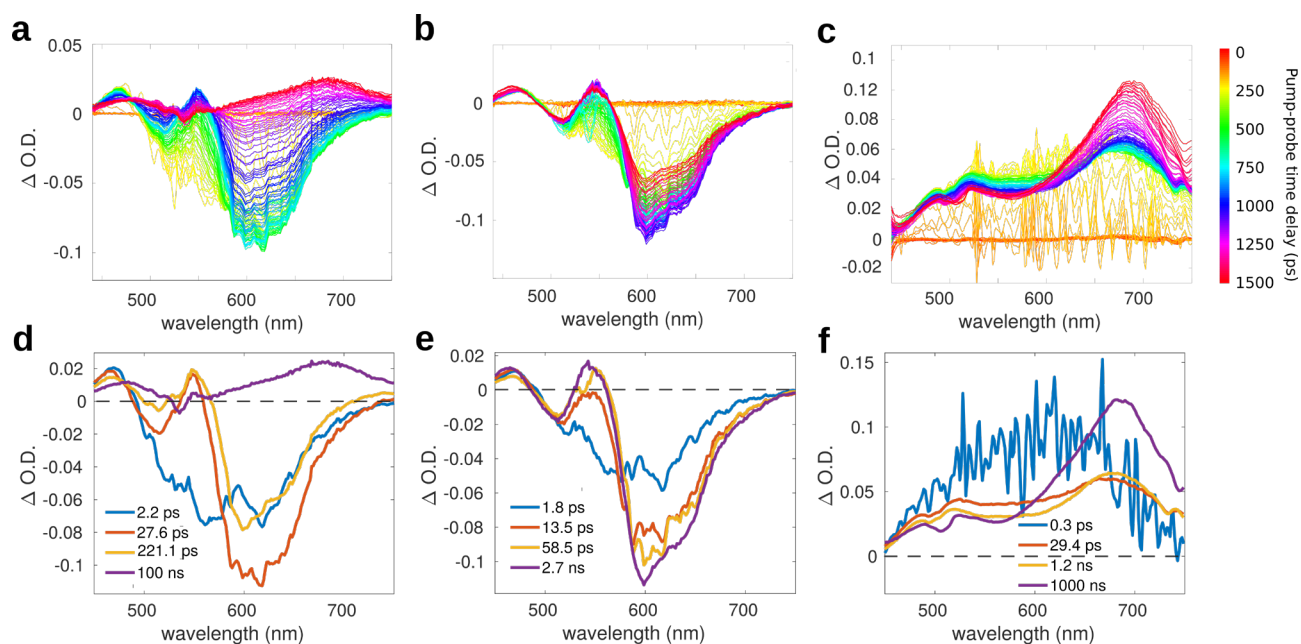
6. Transient spectroscopy

Fig. S12. Transient spectra of compound **3** (panel a, λ_{exc} = 530 nm), **4** (panel b, λ_{exc} = 530 nm) and **5** (panel c, λ_{exc} = 400 nm) in chloroform. Panels d, e, and f report the respective EADS obtained from global analysis.
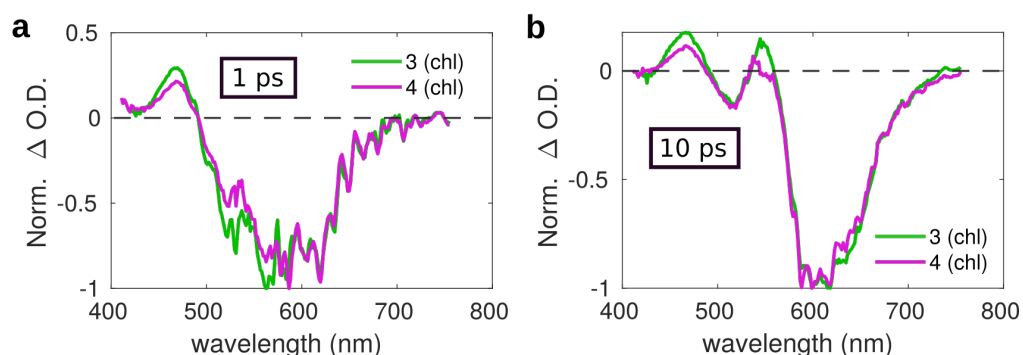

Fig. S13. Comparison between the transient spectra of compound **3** (green lines) and **4** (violet lines) in chloroform registered at a pump-probe delay of 1ps (a) and 10 ps (b).

Single wavelength kinetics of compound **3** are shown in Fig. S14, at five different wavelengths (one for each panel). In each panel the comparison between the two solvents (toluene and chloroform) is presented, showing a faster excited state dynamics in case of toluene.

The comparison between single wavelength kinetics recorded at 517 nm and 615 nm of compounds **3** and **4** is shown in Fig. S15, in case of toluene (a) and chloroform (b). In case of compound **3** a fast component is associated to the energy/electron transfer to the fullerene, with the growth of the positive signal, which lasts until the longest pump-probe delay. In case of compound **4** the decay toward zero represents the slow recovery of its ground state (full recovery is not observed within the experimental time-scale).
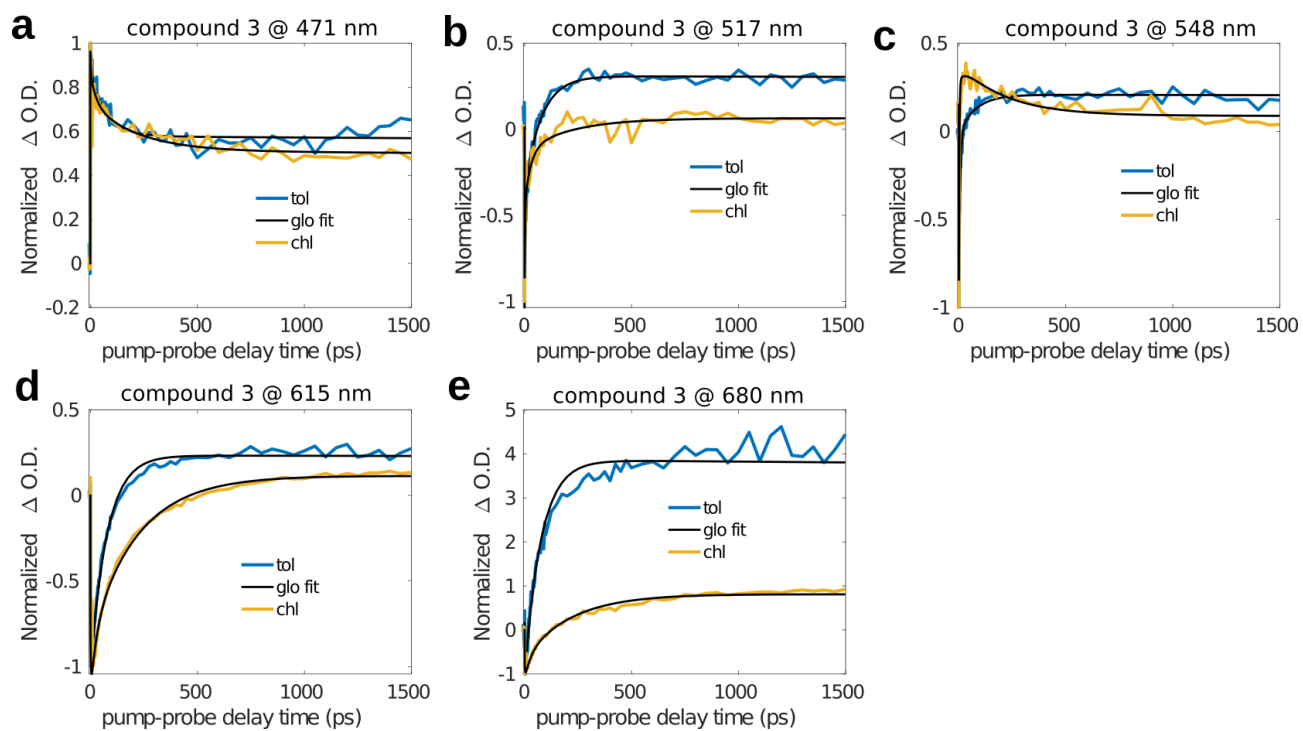
Fig. S14. Single wavelength kinetics of compound **3** at five different wavelengths: comparison between the two solvents.
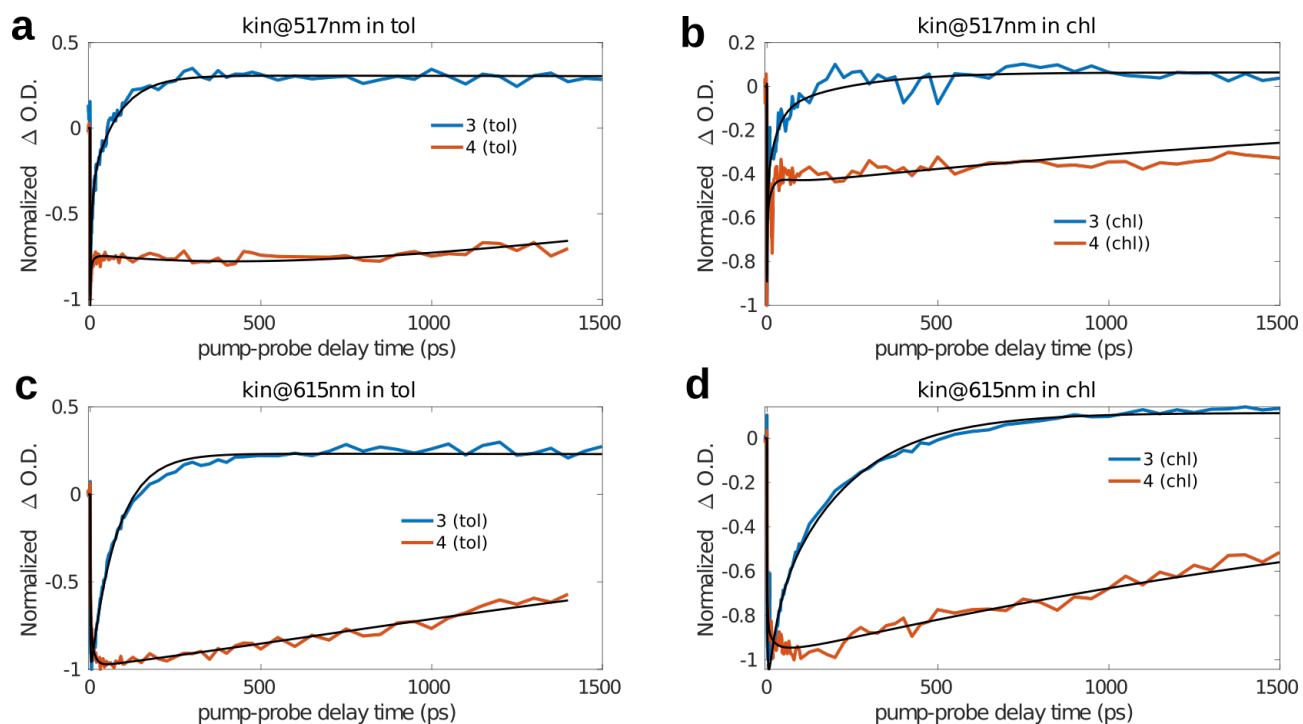

Figure S15. Comparison between single wavelength kinetics of compounds **3** and **4** at 517 nm (a, b) and 615 nm (c, d) in toluene (left) and chloroform (right).
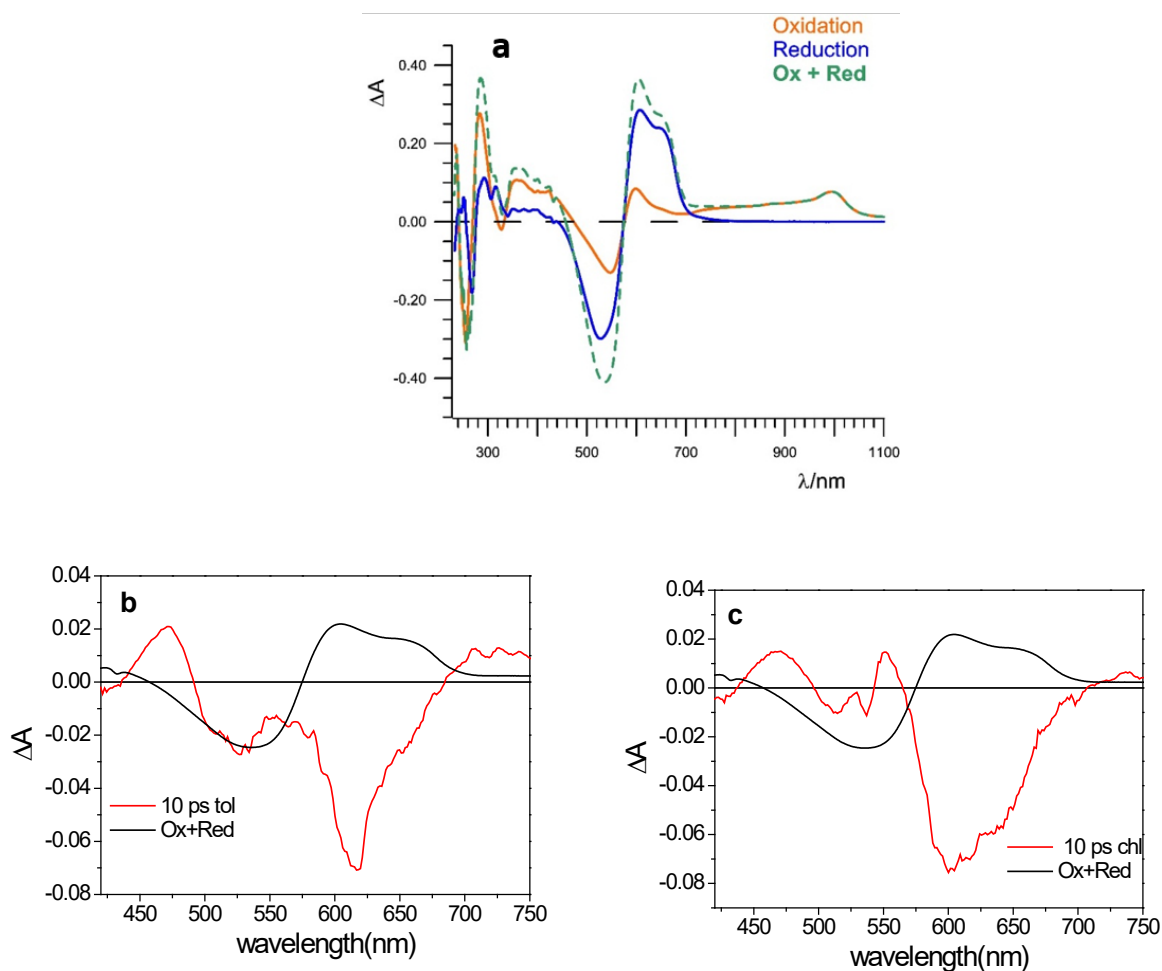
Fig. S16. a) UV-Vis-NIR difference spectra of dyad **3** obtained from spectroelectrochemistry experiments. Difference spectrum of the one-electron reduced species (blue line) at -0.85 V (vs SCE); difference spectrum of the one-electron oxidized compound (orange line) at 1.10 V; spectrum obtained as the combination of the oxidized and reduced species (green dotted line), to mimic the concomitant generation of the reduced acceptor and oxidized donor moiety, for comparison purposes with the transient absorption data reported in the bottom part of the Figure.

Panels b) and c) report the comparison between the pump-probe spectra acquired at 10 ps pump-probe delay and the combination oxidation+reduction spectrum in toluene (b) and chloroform (c).

References for Supplementary Information

1. S. A. Herbert and G. E. Arnott, *Org. Lett.*, 2010, **12**, 4600–4603.

2. D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259–271.

3. S. Mathai, T. A. Smith, and K. P. Ghiggino, *Photochem. Photobiol. Sci.*, 2007, **6**, 995.

4. R. W. Redmond and J. N. Gamlin, *Photochem. Photobiol.*, 1999, **70**, 391–475.