Supporting information

for

Stabilising the Lowest Energy Charge-Separated State in a {Metal Chromophore - Fullerene} Assembly: A Tuneable Panchromatic Absorbing Donor-Acceptor Triad.

Maria A. Lebedeva,[a,b*] Thomas W. Chamberlain,[a,c] Paul A. Scattergood,[d] Milan Delor,[d] Igor V. Sazanovich,[d,e] E. Stephen Davies,[a] Mikhail Suyetin, [a] Elena Besley,[a] Martin Schröder,[a,f] Julia A. Weinstein,[d*] and Andrei N. Khlobystov[a,g*]

[a] *School of Chemistry, University of Nottingham, Nottingham, NG7 2RD, UK*

[b] *Department of Materials, University of Oxford, 16 Parks Road, Oxford, OX1 3PS, UK*

[c] *School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK*

[d] *Department of Chemistry, University of Sheffield, S3 7HF, UK*

[e] *Laser for Science Facility, Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Oxfordshire, OX11 0QX, UK*

[f] *School of Chemistry, University of Manchester, Oxford Road, Manchester, UK, M13 9PL, UK*

[g] *Nottingham Nanotechnology & Nanoscience Centre, University of Nottingham, University Park, Nottingham, NG7 2RD, UK.*

e-mail: maria.lebedeva@materials.ox.ac.uk; Julia.weinstein@sheffield.ac.uk; Andrei.khlobystov@nottingham.ac.uk

1. Experimental section

C_{60} (99.5 %) was purchased from SES Research. CH_2Cl_2 was freshly distilled over CaH_2 before use. 4'-methyl-2,2'-bipyridine-4-carboxaldehyde[i] and $Pt(DMSO)_2Cl_2$ were synthesised according to the literature reported procedures. All other reagents and solvents were purchased from Aldrich and used without further purification. Infra-red spectra were measured as KBr discs or as solutions in the suitable solvents using a Nicolet Avatar 380 FT-IR spectrometer over the range 400-4000 cm^{-1}. ^1H and ^{13}C NMR spectra were obtained using Bruker DPX 300, Bruker DPX 400, Bruker AV(III) 400 or Bruker AV(III) 500 spectrometers. Mass spectrometry was carried out using a Bruker microTOF spectrometer and a Bruker ultraFlexIII MALDI TOF spectrometer. UV-vis spectra were measured using a Lambda 25 Perkin Elmer spectrometer. EPR spectra were obtained on a Bruker EMX EPR spectrometer.

Cyclic voltammetry.

Cyclic voltammetric studies were carried out using an Autolab PGSTAT20 potentiostat, using a three-electrode arrangement in a single compartment cell. A glassy carbon working electrode, a Pt wire secondary electrode and a saturated calomel reference electrode (chemically isolated from the test solution *via* a bridge tube containing electrolyte solution and fitted with a porous Vycor frit) were used in the cell. Experiments were performed under an atmosphere of argon and in anhydrous solvents. Sample solutions were prepared under an atmosphere of argon using Schlenk line techniques and consisted of a 0.2 M $[^nBu_4N][BF_4]$ solution as the supporting electrolyte and a 0.5-1 mM solution of the test compound. Redox potentials were referenced *vs*. the Fc^+/Fc couple, which was used as an internal standard. Compensation for internal resistance was not applied.

UV/vis spectroelectrochemistry.

UV/vis spectroelectrochemical experiments were carried out with an optically transparent electrochemical (OTE) cell (modified quartz cuvette, optical pathlength 0.5mm). A three-electrode configuration, consisting of a Pt/Rh gauze working electrode, a Pt wire secondary electrode (in a fritted PTFE sleeve) and a saturated calomel electrode (chemically isolated from the test solution via a bridge tube containing electrolyte solution and terminated in a porous frit) were used in the cell. The potential at the working electrode was controlled by a Sycopel Scientific Ltd. DD10M potentiostat. UV/vis data was recorded on a Perkin Elmer

Lambda 16 spectrometer. The cavity was purged with nitrogen gas and temperature control at the sample was achieved by flowing cooled nitrogen gas across the surface of the cell. Sample solutions were prepared under an atmosphere of argon using Schlenk line techniques and consisted of a 0.2 M [$^{n}Bu_4N$][BF_4] solution as the supporting electrolyte and a 0.25 mM solution of the test compound. The test species in solution was reduced at constant potential and the redox process was considered complete when consecutive spectra were identical. The reversibility of the process was investigated by applying a potential at the working electrode sufficient to re-oxidise the electrogenerated product. The process was considered to be reversible, under the conditions of the experiment, if the spectral profile of the starting material was reproduced.

Bulk electrolysis.

Bulk electrolysis experiments, at a controlled potential, were carried out using a two-compartment cell. A Pt/Rh gauze basket working electrode was separated from a wound Pt/Rh gauze secondary electrode by a glass frit. A saturated calomel electrode was bridged to the test solution through a Vycor frit that was orientated at the centre of the working electrode. The working electrode compartment was fitted with a magnetic stirrer bar and the test solution was stirred rapidly during electrolysis. Each solution contained [NBu_4][BF_4] (0.2 M) as the supporting electrolyte and the compound under investigation (5 mL, 1 mM) and was prepared using Schlenk line techniques.

Computational method.

Molecular mechanics simulations have been performed by the Forcite[ii] program using the Universal force field.[iii] The partial atomic charges have been obtained using the QEq technique[iv] originally developed by Rappé and Goddard. The geometry optimization procedure has been performed using steepest descent algorithm.

Femtosecond TRIR studies were performed in the Central Laser Facility, Rutherford Appleton Laboratory, UK, ULTRA[v] facility. Briefly, the IR spectrometer comprised of two synchronized 10 kHz, 8 W, 40 fs and 2 ps Ti:Sapph oscillator/regenerative amplifiers (Thales), which pump a range of optical parametric amplifiers (TOPAS). A portion of the 40 fs Ti:Sapph beam was used to generate tuneable mid-IR probe light with ca. 400 cm^{-1} bandwidth. The instrumental response function for TRIR measurements is approx. 250 fs. The probe and pump beam diameters at the sample were ca. 70 and 120 μm, resp., the pump

energy at the sample was 1 to 1.5 μJ. Changes in IR absorption spectra were recorded by three HgCdTe linear-IR array detectors on a shot-by-shot basis. All experiments were carried out in Harrick cells with 2 mm thick CaF_2 windows and 500 to 950 μm path length; typical optical density of 0.5 to 1 at 400 nm. All samples were mounted on a 2D-raster stage and solutions were flowed to ensure photostability.

Picosecond transient absorption experiments were performed on a home-built pump-probe setup. The fundamental output (~ 3 mJ, 20 ps, 10 Hz, 1064 nm) of a ps mode-locked Nd:YAG laser PL2251 (EKSPLA) was passed through a computer-controlled optical delay line (made of IMS600 linear stage from NEWPORT; 60 cm travel range), and focused with a 0.5 m lens into a 10 cm cell with D_2O to generate a picosecond super-continuum, which served as a probe beam. The broadband super-continuum beam was split with a beam splitter into signal and reference beams of equal intensity. Both signal and reference beams were passed through the sample one above the other, each focused into a ~ 0.5mm spot on the sample. Afterwards the signal and reference beams were focused with an achromatic condenser onto the entrance slit of the spectrograph (a Hilger & Watts 30 cm monochromator home-converted into a spectrograph by replacing the grating, exit flat mirror, removing exit slit, and fitting a CCD mounting adaptor). Both signal and reference beams were detected with a CCD camera (ANDOR iDus, DV420A) operated in the dual-track mode. The excitation beam was focused into 1 mm spot on the sample, with the pulse energy of 120 μJ at the sample. The pump and the signal probe beams were overlapped at the sample at small angle. The instrumental response function duration of the setup is estimated to be ca. 27 ps. The operation of the setup and the data acquisition process are controlled by custom-developed software. All the measurements were performed in quartz cells with a 2 mm path length; solutions were flown through the cell to ensure photo-stability.

Femtosecond transient absorption experiments in the near-infrared region were performed on the same setup as the one employed in TRIR experiments, with the only major difference being the probe light source. For the NIR TA experiments, a signal output of a TOPAS OPA, centered at ca. 1200 nm was used as the probe, bypassing the DFG stage. The NIR probe light was detected with the same combination of spectrographs and MCT detectors as those used in TRIR experiments. The probe light polarisation at the sample was set to magic angle with respect to the excitation beam polarisation to avoid rotational relaxation dynamics.

The data were detected in several sets of ~40-nm windows between 1020 and 1200 nm, which permitted analysis of excited state dynamics associated with this spectral region. We

note that the probe light has very low intensity in this region, and therefore spectral shape can not be analysed and the data should be considered as a "single color" experiment. The dynamics, on the other hand, has been reproduced reliably across the spectral range, and under different experimental conditions, varying the pump power and the concentration of the sample, and the position of the spectrograph within the stated range.

Synthetic procedures.

4'-methyl-2,2'-bipyridine-4-carboxaldehyde (6).

4,4'-dimethyl-2,2'-bipyridine (5 g, 0.027 mol) and selenium dioxide (3.3 g, 0.029 mol) were degassed with Ar and dissolved in degassed 1,4-dioxane (180 mL). The resulting mixture was heated to reflux for 24 h and the resulting solution was filtered hot. The filtrate was concentrated, redissolved in ethyl acetate (200 mL) and filtered to remove additional solid material. The filtrate was extracted with 1M Na_2CO_3 (2 x 100 mL) to remove additional carboxylic acid and 0.3 M $Na_2S_2O_3$ (3 x 100 mL) to form the aldehyde bisulfite. The aqueous bisulfite fractions were combined, adjusted to pH 10 with Na_2CO_3 and extracted with CH_2Cl_2 (4 x 100 mL). The organic fractions were combined and concentrated to dryness to give 2.96 g (55 %) of the product as a white powder.

^{1}H NMR ($CDCl_3$, δ, ppm): 10.19 (s, 1H, Ar H), 8.90 (d, 1H, Ar H, J=4.9 Hz), 8.84 (s, 1H, Ar H), 8.58 (d, 1H, Ar H, J=4.9 Hz), 8.29 (s, 1H, Ar H), 7.73 (s, 1H, Ar H, J=4.6 Hz), 7.21 (d, 1H, Ar H, J=4.6 Hz), 2.47 (s, 3H, CH_3).

N-((3,5-di-tert-Butylphenyl)methyl)glycine methyl ester (4).

Glycine methyl ester hydrochloride (0.37 g, 2.96 mmol) and 3,5-di-tert-butylbenzaldehyde (0.50 g, 2.29 mmol) were degassed with Ar and suspended in dry DCM (15 mL). Et_3N (0.41 mL, 0.30 g, 2.97 mmol) was added, and resulting solution was stirred at room temperature for 17 hours in the presence of 4 Å molecular sieves. The molecular sieves and resulting precipitate were removed by filtration, the filtrate was concentrated to 10 mL, and $Na[B(OAc)_3H]$ (0.63 g, 2.97 mmol) and glacial acetic acid (2 mL) were added, and the resulting suspension was left to stir at room temperature for 17 hours. The solvent was then removed under reduced pressure and the resulting mixture dissolved in MeOH (5 mL), cooled to 0 ºC, and $NaHCO_3$ solution was slowly added until the mixture reached a pH of 7. The resulting solution was extracted in DCM (4 x 15 mL), the organic fractions combined, washed with water (10 mL) and dried over $MgSO_4$. After removal of $MgSO_4$ the resulting

solution was concentrated and purified by column chromatography (silica gel, petroleum ether/ethyl acetate 10:1, then 10:2) to give the product (0.49 g, 73 %) as a colourless oil.

^{1}H NMR (400 MHz, 297 K, $CDCl_3$, δ, ppm): 7.36 (s, 1H, Ar H), 7.20 (s, 2H, Ar H), 3.82 (s, 2H, CH_2), 3.75 (s, 3H, $COOCH_3$), 3.49 (s, 2H, CH_2), 1.36 (s, 18H, $C(CH_3)_3$.

^{13}C NMR (100 MHz, 297 K, $CDCl_3$, δ, ppm): 172.98 ($COOCH_3$), 150.88, 138.50, 122.46, 121.25 (Ar C), 54.03, 51.73, 50.14, 34.82, 31.52.

ESI MS (m/z): 292.2 $(M+H)^+$.

N-((3,5-di-tert-Butylphenyl)methyl)glycine (5).

N-((3,5-di-tert-Butylphenyl)methyl)glycine methyl ester (0.49 g, 1.68 mmol) was dissolved in MeOH (10 mL), NaOH (150 mg, 3.75 mmol) was added, and the reaction mixture was left to stir at room temperature for 72 hours. The solvent was removed under reduced pressure, the resulting solid was dissolved in water (2 mL), and 1M HCl solution was added dropwise to adjust the pH to 6.7. The resulting white precipitate was filtered, washed with water (3 x 5 mL) followed by acetone (1 mL) and dried in air to give the product (0.32 g, 70 %) as a white powder.

^{1}H NMR (400 MHz, 297 K, $CDCl_3$, δ, ppm): 9.80 (broad s, 1H, COOH), 7.35 (s, 2H, Ar H), 7.30 (s, 1H, Ar H), 3.83 (s, 2H, CH_2), 3.40 (s, 2H, CH_2), 1.24 (s, 18H, $C(CH_3)_3$).

^{13}C NMR (100 MHz, 297 K, $CDCl_3$, δ, ppm): 170.55 (COOH), 151.46, 130.76, 124.25, 122.87 (Ar C), 51.19, 48.35, 34.81, 31.35.

ESI MS (m/z): 276.2 $(M-H)^-$.

IR (KBr, ν, cm^{-1}): 3422 (m, OH), 2964 (s), 2360 (w), 1614 (s, C=O), 1389 (s), 1296 (w), 1249 (m), 1203 (m), 1076 (w), 881 (m), 715 (w), 527 (m).

4-Methyl,4'-(2-(N-(3,5-di-tert-butylphenylmethyl))fulleropyrrolidine)-bipyridine (1).

C_{60} fullerene (100 mg, 0.139 mmol), N-((3,5-di-tert-butylphenyl)methyl)glycine (46 mg, 0.167 mmol) and 4-formyl-4'-methylbipyridine (33 mg, 0.167 mmol) were degassed with Ar and dissolved in dry toluene (60 mL). The resulting mixture was sonicated for 15 minutes, degassed using Ar for 15 minutes and then heated to reflux for 2 hours. The solvent was then

removed under reduced pressure and the resulting solid purified by column chromatography (silica gel, toluene, then toluene/ethyl acetate 99:1). Further purification was carried out by suspending the solid in MeOH (20 mL), filtering, washing with MeOH (30 mL) and drying under vacuum to give the desired product as a black solid (68 mg, 43 %).

^{1}H NMR (400 MHz, 297 K, $CDCl_3$, δ, ppm): 8.97 (s, 1H, Ar H), 8.80 (d, 1H, Ar H, J=5.0 Hz), 8.60 (d, 1H, Ar H, J=5.0 Hz), 8.33 (s, 1H, Ar H), 8.02 (s, 1H, Ar H), 7.54 (d, 2H, Ar H, J=1.8 Hz), 7.46 (t, 1H, Ar H, J=1.8 Hz), 5.38 (s, 1H, CH), 4.98 (d, 1H, CH_2, J=9.6 Hz),4.51 (d, 1H, CH_2, J=13.7), 4.28 (d, 1H, CH_2, J=9.6), 3.84 (d, 1H, CH_2, J=13.7), 2.47 (s, 3H, CH_3), 1.42 (s, 18H, $C(CH_3)_3$).

^{13}C NMR (125 MHz, 297 K, $CDCl_3$, δ, ppm): 156.11, 153.51, 152.36, 152.03, 151.23, 149.40, 147.38, 147.33, 146.33, 146.30, 146.27, 146.23, 146.14, 146.02, 146.00, 145.77, 145.71, 145.60, 145.54, 145.43, 145.39, 145.34, 145.32, 145.20, 144.74, 144.51, 144.46, 144.38, 143.13, 143.03, 142.73, 142.62, 142.55, 142.30, 142.27, 142.21, 142.16, 142.13, 142.07, 142.04, 141.94, 141.86, 141.75, 141.69, 140.25, 140.23, 140.19, 139.51, 137.91, 137.22, 136.54, 136.29, 136.13, 135.91, 129.06, 128.25, 125.32, 122.86, 121.60, 79.83, 76.04, 68.91, 66.46, 56.80, 34.98, 31.61, 21.73, 21.50.

UV-Vis (CH_2Cl_2): λ_{max} (ε x 10^{-3}/dm^{-3} mol^{-1} cm^{-1}): 706 (0.294), 431 (3.617).

IR (KBr, ν, cm^{-1}): 2958 (s), 1593 (s), 1429 (m), 1317 (w), 1225 (m), 1181 (m), 825 (m), 527 (s).

MALDI-TOF MS (DCTB/MeCN, m/z): 1133.1 (M^-).

4-Methyl,4'-(2-(N-(3,5-di-tert-butylphenylmethyl))fulleropyrrolidine)-bipyridine Pt dichloride (2).

4-Methyl,4'-(2-(N-(3,5-di-tert-butylphenylmethyl))fulleropyrrolidine)-bipyridine (20 mg, 0.018 mmol) and $Pt(DMSO)_2Cl_2$ (8 mg, 0.019 mmol) were degassed with Ar and dissolved in degassed $CHCl_3$ (15 mL). The resulting mixture was heated to reflux under an Ar atmosphere for 4 hours. The solvent was then removed under reduced pressure using Schlenk line techniques, and the resulting solid was purified by column chromatography (silica gel, under N_2 pressure, DCM, then DCM/MeOH 99.5:0.5). The product fraction was concentrated using the Schlenk line techniques and dried under vacuum to give the product (22 mg, 89 %) as a brown solid.

^{1}H NMR (400 MHz, 297 K, $CDCl_3$, δ, ppm): 9.79 (d, 1H, Ar H, J=6 Hz), 9.49 (d, 1H, Ar H, J=6Hz), 8.55 (s, 1H, Ar H), 8.10 (s, 1H, Ar H), 7.88 (s, 1H, Ar H), 7.51 (s, 3H, Ar H), 7.34 (d, 1H, Ar H, J=5.5 Hz), 5.50 (s, 1H, CH pyrrolidine), 5.07 (d, 1H, CH_2, J=9.8 Hz), 4.48 (d, 1H, CH_2, J=13.8 Hz), 4.40 (d, 1H, CH_2, J=9.8 Hz), 3.98 (d, 1H, CH_2, J=13.8 Hz), 2.58 (s, 3H, CH_3), 1.44 (s, 18 H, $C(CH_3)_3$).

^{13}C NMR (125 MHz, 297 K, $CDCl_3$, δ, ppm):162.65, 159.24, 157.32, 156.26, 155.32, 152.99, 152.04, 151.54, 151.24, 150.60, 149.79, 149.17, 147.48, 147.41, 146.43, 146.31, 146.25, 146.12, 146.09, 145.99, 145.85, 145.63, 145.60, 145.52, 145.47, 145.36, 145.27, 145.13, 144.77, 144.70, 144.50, 144.29, 143.24, 143.13, 142.88, 142.78, 142.74, 142.64, 142.21, 142.17, 142.10, 142.00, 141.95, 141.84, 141.77, 141.74, 136.59, 135.80, 135.47, 129.21, 128.91, 128.05, 127.34, 124.17, 122.77, 122.02, 79.16, 75.43, 68.76, 66.62, 56.94, 35.01, 31.65, 31.33, 29.72, 29.58, 22.01.

UV-Vis (CH_2Cl_2): λ_{max} (ε x 10^{-3}/dm^{-3} mol^{-1} cm^{-1}): 706 (0.161), 431 (4.987), 397 (11.200).

IR (KBr, ν, cm^{-1}): 2960 (s), 1620 (m), 1429 (m), 1361 (w), 1247 (m), 831 (w), 713 (w), 527 (m).

MALDI-TOF MS (DCTB/MeCN, m/z): 1398.1 (M^-).

Pt 3,5-di-*tert*-Butylcatecholate DMSO complex (8).

NaOH (12 mg, 0.300 mmol) was dissolved in MeOH (5 mL) and thoroughly degassed with Ar. 3,5-di-tert-Butyl catechol (33 mg, 0.149 mmol) was added, and the resulting mixture was stirred at room temperature for 10 minutes. $PtCl_2(DMSO)_2$ complex (30 mg, 0.071 mmol) was added and the mixture was stirred at room temperature for 17 hours under an Ar atmosphere. The solvent was then removed under reduced pressure, and the resulting oil was purified by column chromatography (silica gel, DCM, then DCM/MeOH 98:2) to give the product (60 mg, 71 %) as yellow oil.

^{1}H NMR (400 MHz, 297 K$CDCl_3$, δ, ppm): 6.67 (d, 1H, Ar H, J=2.3 Hz), 6.57 (d, 1H, Ar H, J=2.3 Hz), 3.56 (s, 6H, $(CH_3)_2SO$), 3.54 (s, 6H, $(CH_3)_2SO$),1.42 (s, 9H, $(CH_3)_3C$), 1.28 (s, 9H, $(CH_3)_3C$).

ESI MS (m/z): 572 $(M+H)^+$, 594 $(M+Na)^+$, 1165 $(2M+Na)^+$.

4-Carboxaldehydo-4'-methyl-2,2'-bipyridine-Pt-3,5-di-tert-butyl catecholate (9).

To a solution of 4-formyl-4'-methyl-2,2'-bipyridine (100 mg, 0.54 mmol) in dry DMF (30 mL) a solution of Pt 3,5-di-tert-butylcatecholate DMSO complex (320 mg, 0.56 mol) in dry DMF (5 mL) was added and the resulting mixture was degassed with Ar for 30 minutes and then heated to 120°C for 17 hours. The solvent was then removed under reduced pressure and the resulting mixture was purified by column chromatography (silica gel, $CHCl_3$/MeOH 98:2, then 96:4) to give the product (18 mg, 5 %) as a dark-blue solid.

^{1}H NMR (400 MHz, 297 K, $CDCl_3$, δ, ppm): 10.22 (s, 1H, CHO), 9.68 (d, 1H, CH pyridine, J=5.6 Hz), 9.20 (d, 1H, CH pyridine, J=5.6 Hz), 8.92 (d, 1H, CH pyridine, J=5.0 Hz), 8.62 (d, 1H, CH pyridine, J=5.0 Hz), 8.31 (s, 1H, CH pyridine), 7.59 (s, 1H, CH pyridine), 6.96 (d, 1H, CH catechol, J=2.4 Hz), 6.25 (d, 1H, CH catechol, J=2.4 Hz), 2.65 (s, 3H, CH_3), 1.46 (s, 9 H, $C(CH_3)_3$), 1.44 (s, 9 H, $C(CH_3)_3$).

MALDI-TOF MS (DCTB/MeCN, m/z): 613.1 (M^+).

4-Methyl,4'-(2-(N-(3,5-di-tert-butylphenylmethyl))fulleropyrrolidine)-2,2'-bipyridine Pt 3,5-di-tert-butyl catecholate (3).

C_{60} (35 mg, 0.049 mmol), N-((3,5-di-tert-butylphenyl)methyl)glycine (13.5 mg, 0.049 mmol) and 4-formyl-4'-methyl-2,2'-bipyridine-Pt-3,5-di-tert-butyl catecholate (30 mg, 0.049 mmol) were degassed with Ar and dissolved in a mixture of toluene and acetonitrile (35 mL, 6:1 v/v). The resulting mixture was sonicated for 15 minutes, degassed with Ar for 30 minutes and refluxed for 1.5 hours. The solvent was then removed under reduced pressure, and the resulting mixture was purified by column chromatography (silica gel, using toluene, followed by a mixture of toluene and acetonitrile (97:3 v/v and then 94:6 v/v) to give the product (13 mg, 20 %) as a dark-green solid.

^{1}H NMR (400 MHz, 297 K, CS_2/toluene-d_8, 7:1 v/v, δ, ppm): 9.41 (d, 1H, Ar H, J=5.6 Hz), 8.90 (d, 1H, Ar H, J=4.6 Hz), 8.18 (s, 1H, Ar H), 7.35 (s, 3H, Ar H), 7.31 (s, 1H, Ar H), 6.96 (s, 1H, Ar H), 6.56 (s, 1H, Ar H), 6.53 (s, 1H, Ar H), 6.27 (s, 1H, AR H), 5.06 (s, 1H, CH pyrrolidine), 4.79 (d, 1H, CH_2, J=9.8 Hz), 4.35 (d, 1H, CH_2, J=13.7 Hz), 4.11 (d, 1H, CH_2, J=9.7 Hz), 3.68 (d, 1H, CH_2, J=13.7 Hz), 1.96 (s, 3H, CH_3), 1.47 (s, 9H, $C(CH_3)_3$ catechol), 1.29 (s, 18H, $C(CH_3)_3$), 1.20 (s, 9H, $C(CH_3)_3$ catechol).

^{13}C NMR (125 MHz, 297 K, CS_2/toluene-d_8, 7:1 v/v, δ, ppm): 163.18, 159.59, 156.32, 155.35, 155.11, 152.82, 151.62, 151.34, 151.07, 148.98, 148.33, 148.02, 147.44, 147.24, 146.28, 146.20, 146.18, 146.14, 146.07, 145.94, 145.92, 145.90, 145.78, 145.74, 145.50, 145.46, 145.39, 145.35, 145.33, 145.21, 145.16, 145.08, 144.96, 144.90, 144.58, 144.36, 144.20, 143.07, 143.03, 142.75, 142.63, 142.59, 142.50, 142.13, 142.05, 142.04, 141.96, 141.93, 141.86, 141.81, 141.64, 141.62, 140.34, 140.29, 140.18, 139.91, 137.73, 137.66, 136.37, 135.76, 135.51, 133.77, 122.63, 121.82, 111.22, 110.60, 79.68, 75.20, 68.62, 66.62, 56.93, 34.80, 34.72, 33.89, 32.37, 31.49, 30.42, 30.34.

UV-Vis (DMF): λ_{max} (ε x 10^{-3}/dm^{-3} mol^{-1} cm^{-1}): 587 (6.88), 436 (6.64).

IR (KBr, ν, cm^{-1}): 2957 (s), 2360 (m), 1618 (w), 1438 (m), 1361 (w), 1287 (m), 1243 (m), 979 (m), 810 (w), 527 (m).

MALDI-TOF MS (DCTB/MeCN, m/z): 1547 (M^-).

2. NMR Spectroscopy data.

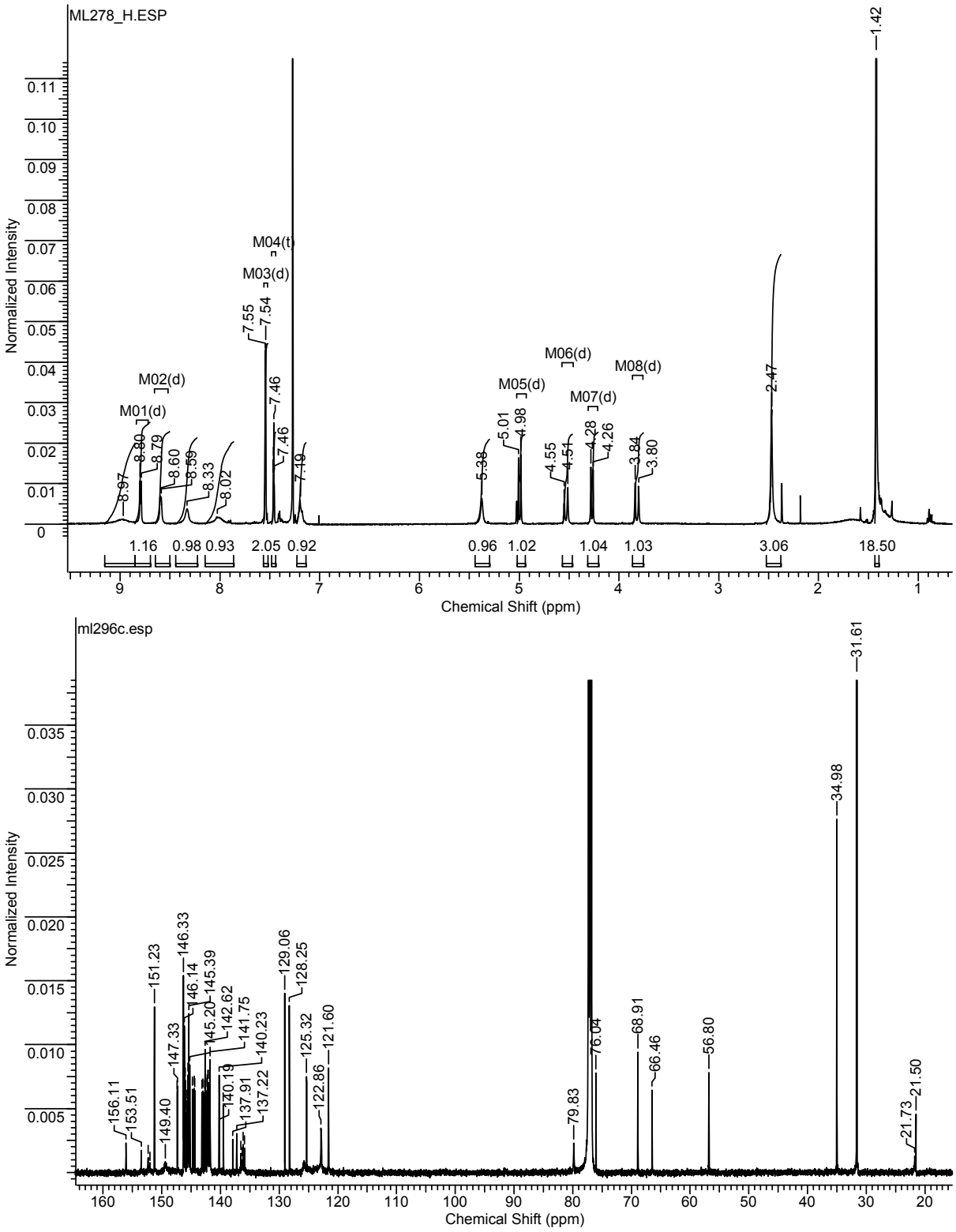


Figure S1. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **1** recorded in $CDCl_3$.

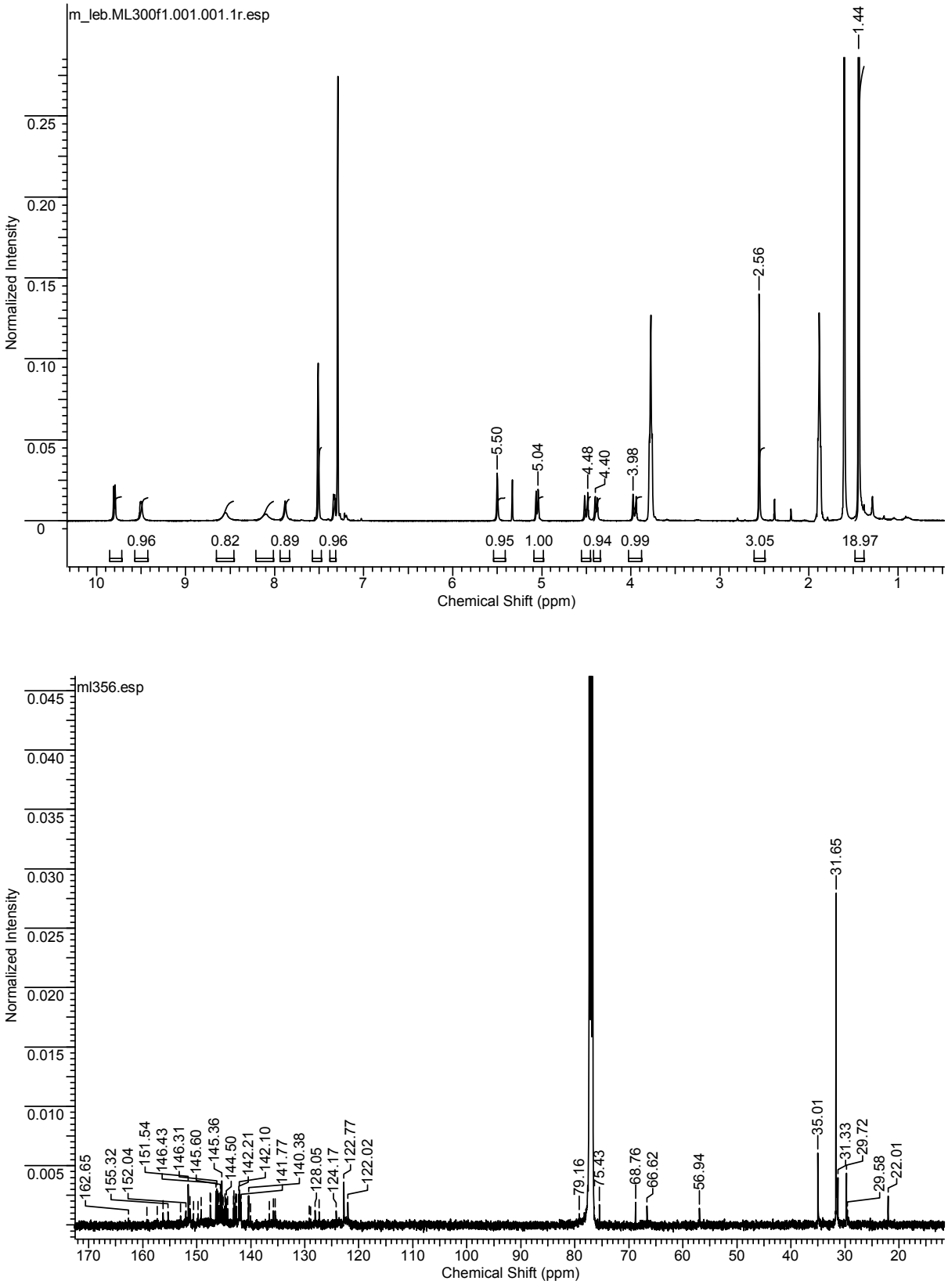


Figure S2. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **2** recorded in $CDCl_3$.

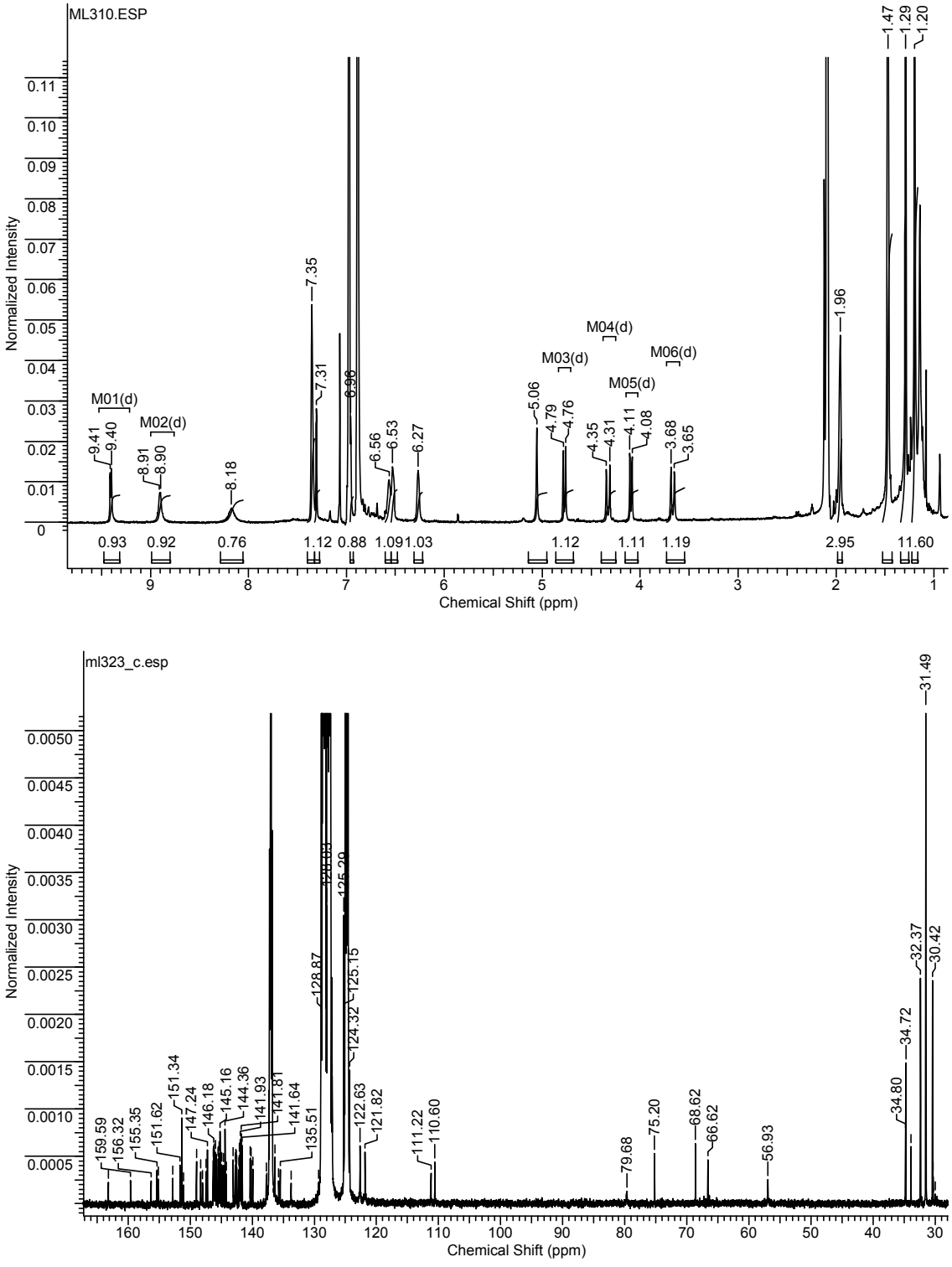


Figure S3. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **3** recorded in CS_2/toluene-d_8 mixture.

3. UV/vis spectroscopy data.

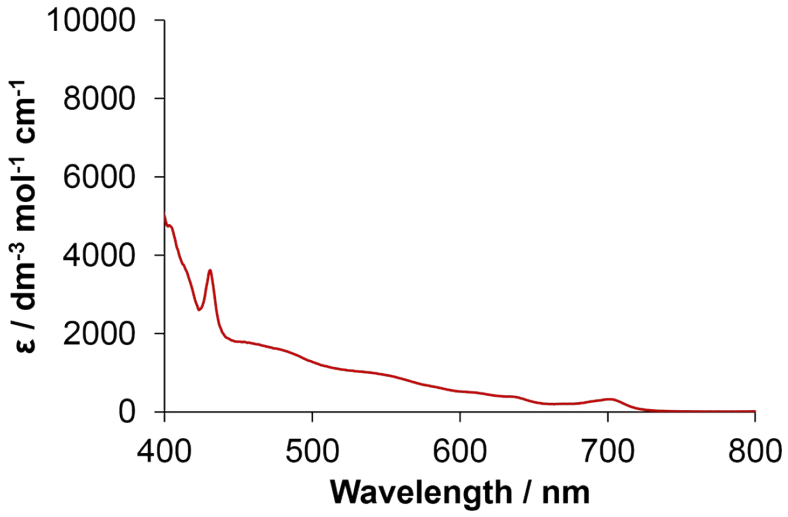


Figure S4. Uv/vis spectrum of **1** (red line) recorded in CH_2Cl_2.

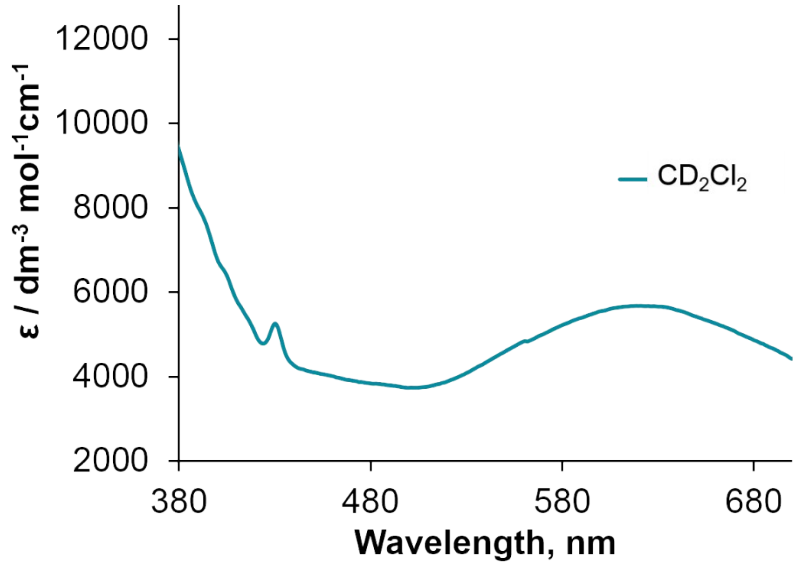


Figure S5. UV/vis absorption spectrum of complex **3** recorded in CD_2Cl_2.

Table S1. Absorption data for complex **3** in different solvents.

Solvent	**Relative polarity[vi]**	**UV/vis: λ, nm (ε x 10^{-3} /dm^{-3} mol^{-1} cm^{-1})**
CS_2	0.065	786 (6.1), 435 (8.1).
Toluene	0.099	725 (5.5), 435 (5.4).
THF	0.207	675 (6.1), 435 (5.4).
CD_2Cl_2	0.259[a]	626 (5.7), 435 (5.4).
Acetone	0.355	617 (6.1), 435 (5.4).
DMF	0.386	600 (5.5), 435 (5.4).

[a] value for CH_2Cl_2 is given instead of CD_2Cl_2

4. Cyclic voltammetry.

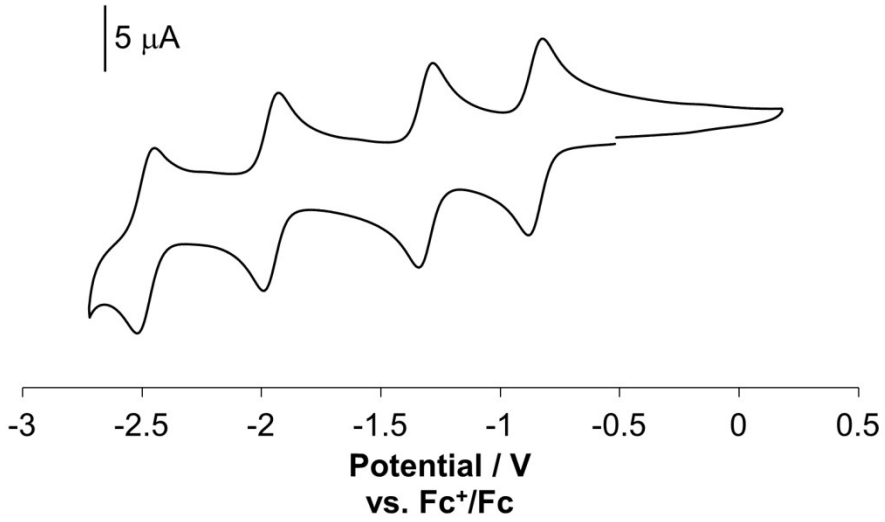


Figure S6. The cyclic voltammogram of **1** in DMF with $[NBu_4^+][BF_4^-]$ (0.2 M) as supporting electrolyte at a scan rate of 0.1 Vs^{-1}.

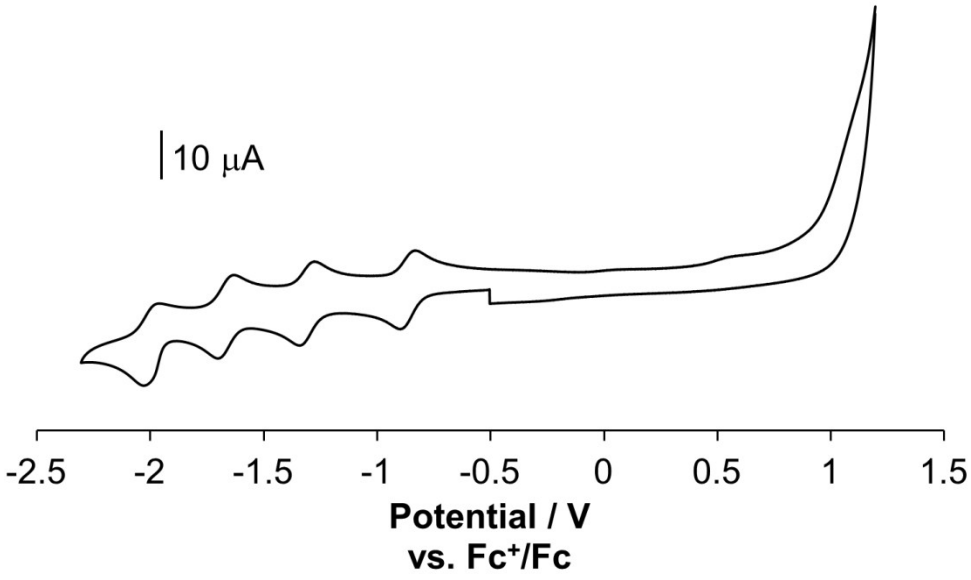


Figure S7. The cyclic voltammogram of **2** in DMF with $[NBu_4^+][BF_4^-]$ (0.2 M) as supporting electrolyte at a scan rate of 0.1 Vs^{-1}.

5. Femtosecond transient absorption data in the near infrared region.

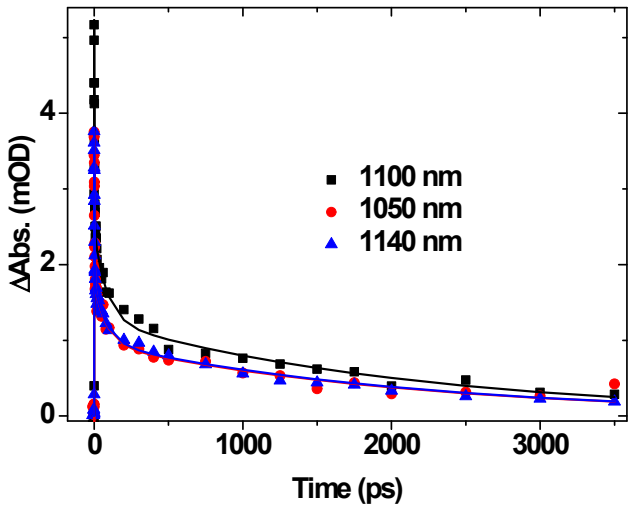
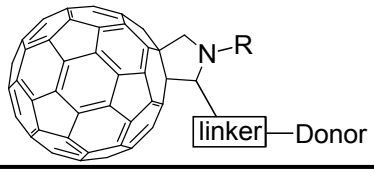
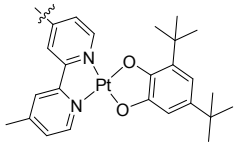
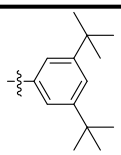
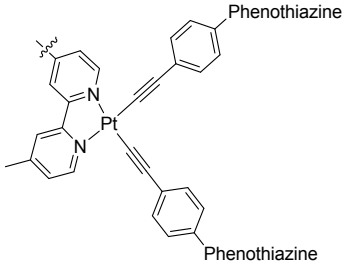
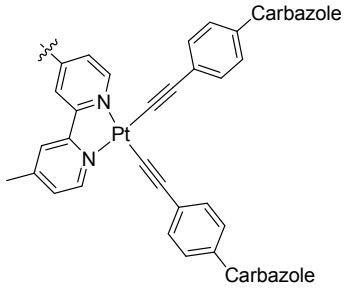
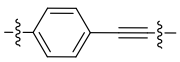
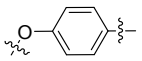
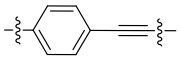
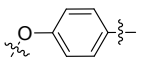


Figure S8. Near-infrared femtosecond transient absorption data for the solution of **3** in DCM at r.t. obtained under 400 nm, ~50fs excitation. Representative kinetic traces at selected wavelengths are shown. Solid lines show the results of global fit to the data across 1020 – 1200 region, with parameters 2(±1) ps, 50(±8) ps, and 1020 (±150) ps.

6. Comparison of photophysical properties of 3 with various structurally related fulleropyrrolidine-donor dyads.

Table S2. Charge transfer processes in fulleropyrrolidine derivatives.



Donor	Linker	R	Lifetime of CCS	Ref.
	-		890 ps in THF	This study
	-	$-C_{12}H_{25}$	Ultrafast charge separation with subsequent gereation of long-lived $^3C_{60}$*	vii
	-	$-C_{12}H_{25}$	Ultrafast charge separation with subsequent gereation of long-lived $^3C_{60}$*	viii
$[Ru(bipy)_3^{2+}][2PF_6^-]$	-	$-CH_3$	No CSS[a] formed	ix
ZnPorphyrin	-	$-CH_3$	No CSS formed	x
ZnPorphyrin		$-CH_3$	60 ps in CH_3CN	x
ZnAzulenocyanine	-	$-CH_3$	No CSS formed	xi
ZnPorphyrin		$-CH_3$	190 ps in 2-MeTHF	xii
Zn Phthalocyanine		$-C_8H_{17}$	890 ps in THF	xiii
p-Tolyl-dioxyboron dipyrrin	-	$-CH_3$	310 ps in	xiv
p-Tolyl-bis(1-hexadecynyl)boron dipyrrin		$-CH_3$	430 ps in PhCN	xv
Cyanine		$-C_8H_{17}$	400 ps in PhCN	xvi
Tetrathiafulvalene (TTF)	-	$-CH_3$	2 ns in PhCN	xvii
Extended TTF	-	3,6,9-trioxadecyl	180 ns in PhCN	xviii
Ferrocene	-	$-CH_3$	No CSS formed	xix
Ferrocene		$-CH_3$	No CSS formed	xix

[a] CSS=Charge-separated state

[i] G. Strouse, J. Schoonover, R. Duesing, S. Boyde, W. Jones and T. Meyer, *Inorg. Chem*., 1995, **34**, 473-487.
[ii] Materials Studio 5.0., Accelrys Software Inc., San Diego, CA 92121, USA.
[iii] A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard III, W. M. Skiff, J. Am. Chem. Soc. 1992, 114, 10024−10035.
[iv] A.K. Rappe and W.A. Goddard III, J. Phys. Chem. 1991, 95, 3358-3363.
[v] Greetham, G.; Burgos, P.; Cao, Q.; Clark, I.; Codd, P.; Farrow, R.; George, M.; Kogimtzis, M.; Matousek, P.; Parker, A.; Pollard, M.; Robinson, D.; Xin, Z.-J.; Towrie, M. *Appl. Spectrosc.*, **2010**, *64*, 1311–1319.
[vi] Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH Publishers, 3rd ed., **2003**
[vii] S.-H. Lee, C. T.-L. Chan, K. M.-C. Wong, W. H. Lam, W.-M. Kwok, V. W.-W. Yam, J. Am. Chem. Soc., 2014, 136, 10041-10052.
[viii] S.-H. Lee, C. T.-L. Chan, K. M.-C. Wong, W. H. Lam, W.-M. Kwok, V. W.-W. Yam, Dalton Trans., 2014, 43, 17624-17634.
[ix] S. Karlsson, J. Modin, H.-C. Becker, L. Hammarström and H. Grennberg, *Inorg. Chem*. 2008, **47**, 7286-7294.
[x] N.V. Tkachenko, H. Lemmetyinen, J. Sonoda, K. Ohkubo, T. Sato, H. Imahori and S. Fukuzumi, *J. Phys. Chem. A*, 2003, **107**, 8834-8844.
[xi] M. Ince, A. Hausmann, M. V. Martínez-Díaz, D. M. Guldi and T. Torres, Chem. Commun., 2012, **48**, 4058–4060.
[xii] A. Kahnt, J. Kärnbratt, L.J. Esdaile, M. Hutin, K. Sawada, H. L. Anderson and B. Albinsson, *J. Am. Chem. Soc*., 2011, **133**, 9863–9871.
[xiii] J.-J. Cid, A. Kahnt, P. Vázquez, D.M. Guldi and T. Torres, *J. Inorg. Biochem*., 2012, **108**, 216–224.
[xiv] C.A. Wijesinghe, M.E. El-Khouly, N.K. Subbaiyan, M. Supur, M.E. Zandler, K. Ohkubo, S. Fukuzumi and F. D'Souza, *Chem. Eur. J*., 2011, **17**, 3147 – 3156.
[xv] R. Ziessel, B. D. Allen, D. B. Rewinska and A. Harriman, *Chem. Eur. J*., 2009, **15**, 7382 – 7393.
[xvi] C. Villegas, E. Krokos, P.-A. Bouit, J. L. Delgado, D.M. Guldi and N. Martín, *Energy Environ. Sci*., 2011, **4**, 679-684.
[xvii] N. Martín, L. Sánchez, M. Á. Herranz, B. Illescas, and D. M. Guldi, *Acc. Chem. Res*., 2007, **40**, 1015–1024.
[xviii] M. C. Díaz, M. A. Herranz, B.M. Illescas and N. Martín, *J. Org. Chem.*, 2003, **68**, 7711-7721.
[xix] D. M. Guldi, M. Maggini, G. Scorrano and M. Prato, *J. Am. Chem. Soc*., 1997, **119**, 974-980.