Supporting Information

Non-covalent versus covalent donor-acceptor systems based on near-infrared absorbing azulenocyanines and C_{60} fullerene derivatives

Mine Ince,[a] Anita Hausmann,[b] M. Victoria Martínez-Díaz,[a] Dirk M. Guldi,*[b] and Tomás Torres,*[ac]

[a] *Departamento de Química Orgánica, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain. Fax: + 34 9 1497 3966; Tel: + 34 9 1497 4151; E-mail: tomas.torres@uam.es*

[b] *Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials, Friedrich-Alexander-University Erlangen-Nuremberg, Egerlandstrasse 3, 91058 Erlangen, Germany. Fax: +49 9131 8528307; Tel: +49 9131 8527341; E-mail: guldi@chemie.uni-erlangen.de*

[c] *IMDEA-Nanociencia, Facultad de Ciencias, Ciudad Universitaria de Cantoblanco, 28049 Madrid (Spain)*

Experimental section

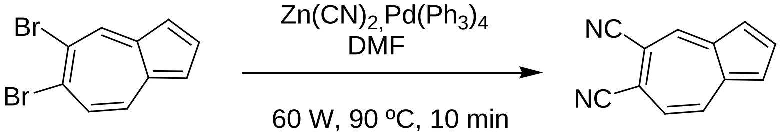
Techniques.

All chemicals were purchased from Aldrich and used without further purification. 5,6-dibromoazulene was prepared using a described procedure.[1] All reactions were followed by TLC employing aluminium sheets coated with silica gel 60 F254 (Merck). ^{1}H NMR spectra were obtained using a Bruker Avance 300 spectrometer. Infrared spectra (IR) were recorded on a Bruker Vector 22. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) MS and highresoltion mass spectrometry (HRMS) spectra were recorded with a Bruker Reflex III spectrometer. Microwave reactions were carried out in a CEM Discover SP-D system.

Photophysical Measurements.

UV/Vis absorption spectroscopy was performed by a Cary 5000 spectrometer (VARIAN) in a 10x10 mm quartz cuvette by using fresh oxygen free solutions. Steady state fluorescence spectra were taken by a FluroMax3 spectrometer (HORIBA) in the visible detection range and by a FluoroLog3 spectrometer (HORIBA) with a IGA Symphony (512 x 1 x 1 μm) detector in the NIR detection range. Transient absorption studies were performed with 387 nm laser pulses of an amplified Ti/sapphire laser system (Model CPA 2101, Clark-MXR Inc.) in the TAPPS - Transient Absorption Pump / Probe System - Helios from Ultrafast Systems with 200 nJ laser energy. Spectroelectrochemistry experiments were performed with a home-built cell and a three-electrode setup: a light-transparent platinum gauze as working electrode, a platinum wire as counter electrode, and a silver wire as quasi reference electrode. Potentials were applied and monitored with a HEKA Elektronik Potentiostat/Galvanostat PG284 and a METROM-Autolab Potentiostat/Galvanostat PGSTAT101. The pathlength of the cell was determined to 2.3 mm. The results are finally shown as differential spectra, i.e. the difference between a spectrum with and without an applied potential. The spectra were recorded with a UV/Vis-spectrometer Cary 5000 (VARIAN).

5,6-dicyanoazulene (6)



In a 10 mL CEM Voyager microwave tube a solution of 5,6-dibromoazulene[1] (100 mg, 0.35 mmol) in DMF (3 mL), $ZnCN_2$ (82 mg, 0.70 mmol), and tetrakis(triphenylphosphine) palladium(0) (25 mg, 0.02 mmol) were added. The reaction tube was sealed and heated to 90 ºC under microwave irradiation with a 10 min hold time, and 60 W maximum power input. The suspension was then poured onto a 2M ammonia solution (100 mL). The mixture was extracted with ethyl acetate (2×100 mL) and the combined organic extracts were washed with brine (20 mL), dried over $MgSO_4$ and evaporated *in vacuo*. The solid residue was purified by column chromatography on silica gel (Hexanes/ethyl acetate, 5:1) to yield 53 mg (85%) of **6** as a green solid.

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.61(s, 1H, ArH), 8.39 (d, J = 9.6 Hz, 1H, ArH), 8.22 (t, J = 3.7 Hz, 1H, ArH), 7.81 (d, J = 3.7 Hz, 1H, ArH), 7.74 (d, J = 3.7 Hz, 1H, ArH), 7.54 (d, J = 9.6 Hz, 1H, ArH).

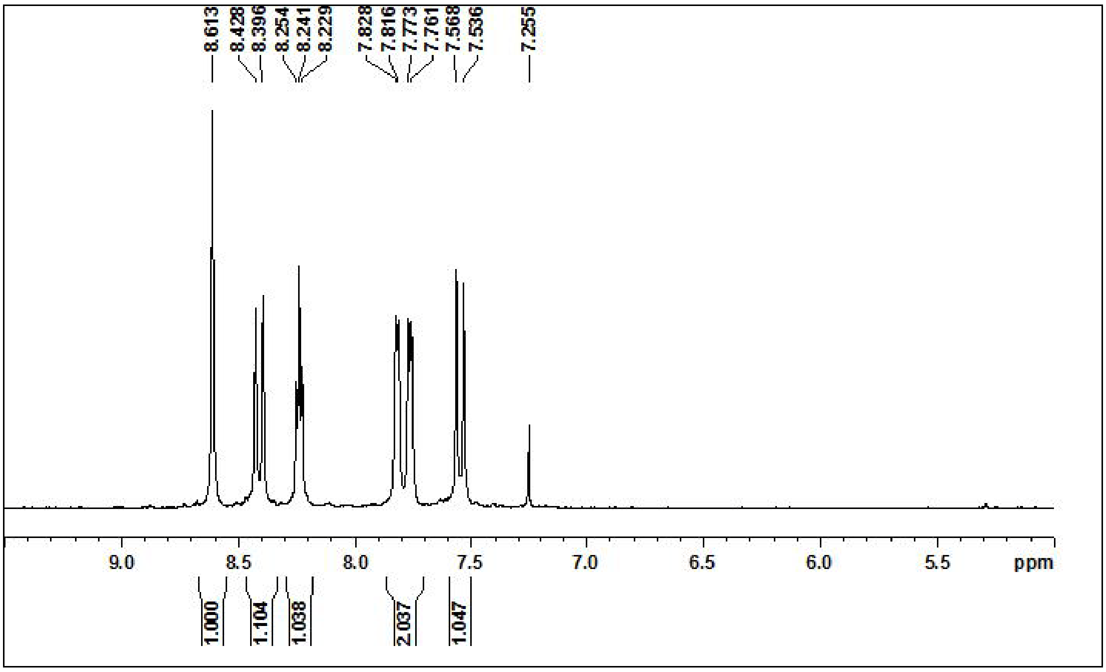
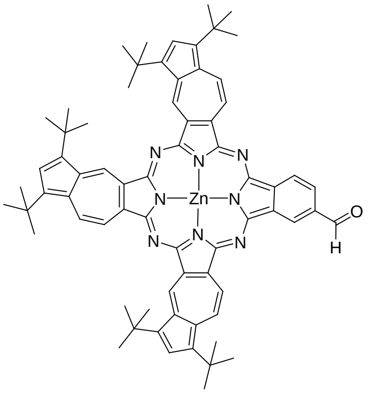


Figure S1. ^{1}H-NMR spectrum for 5,6-dicyanoazulene (**6**) in $CDCl_3$

Formyl-azulenocyanine 4 (mixture of regioisomers)



4

Hydroxymethyl-azulenocyanine **5** (50 mg, 0.045 mmol) was added to a solution of IBX (38 mg, 0.137 mmol) in DMSO (5 mL). The mixture was stirred at room temperature overnight. The reaction was monitored by TLC (Hexanes/dioxane, 3:1) until all the starting azulenocyanine was consumed. Brine was then added and the mixture was extracted with THF. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The solid residue was purified by column chromatography on silica gel (Hexanes/dioxane, 3:1) to give 35 mg (71 %) of a black-greyish solid.

^{1}H-NMR (d_8-THF, 300 MHz) δ (ppm): 11.1-10.7 (m, 3H, ArH), 10.4-10.2 (m, 1H, ArH), 9.4-9.1 (m, 8H, ArH), 8.5- 8.2 (m, 4H, ArH), 2.1-1.5 (m, 54H, alkylH).

UV/Vis (THF): λ_{max} (nm) = 375, 500-1100 (broad);

FT-IR (film) ν (cm^{-1}): 2954, 2924, 2870, 2218, 1690, 1589, 1570, 1408, 1364, 1208, 1046, 995, 893, 716, 689.

MS (MALDI, dithranol), m/z: 1090.5 [M]$^+$. HRMS (MALDI-TOF, DCTB): calc. for $C_{69}H_{70}ZnN_8O$: [M]$^+$: m/z: 1090.4962 found 1090.4968.

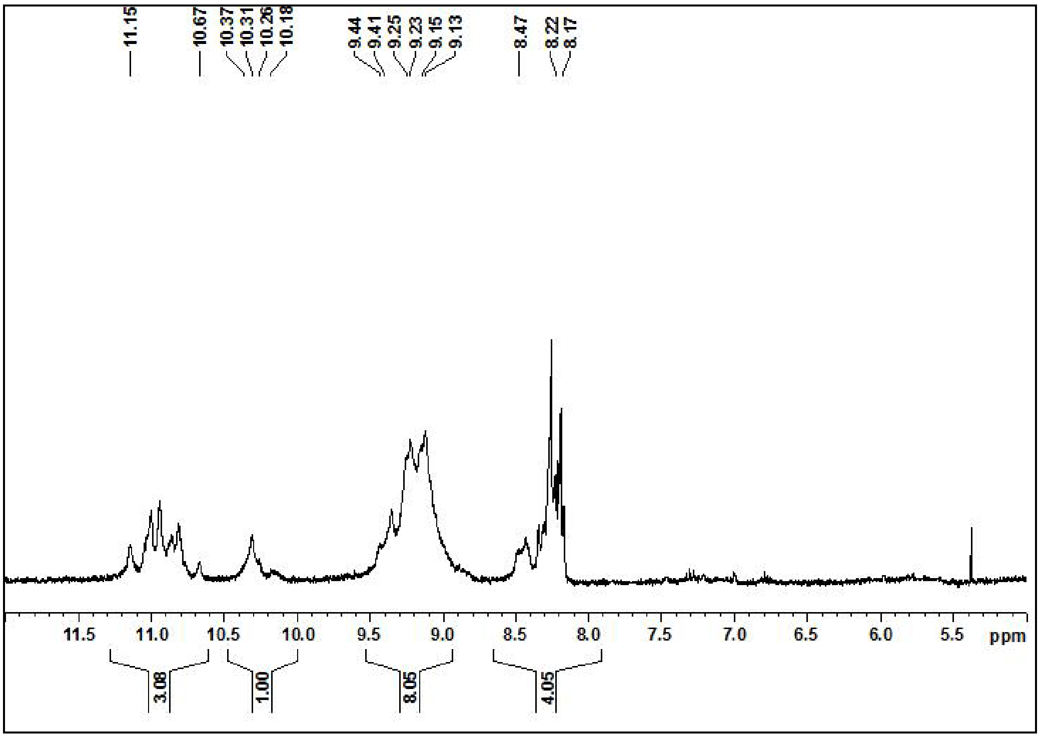


Figure S2. ^{1}H-NMR spectrum for formyl-azulenocyanine **4** in d_8-THF

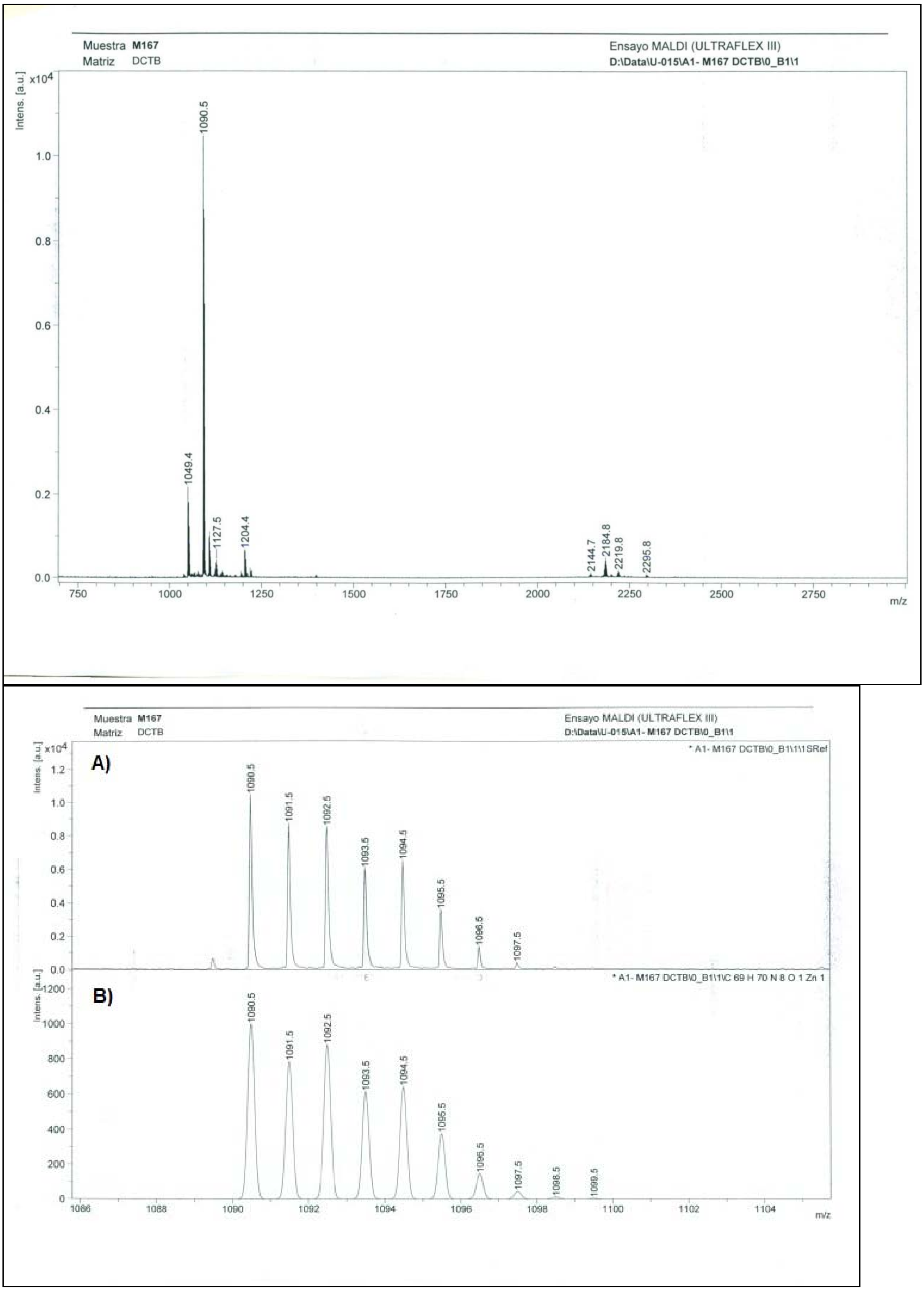
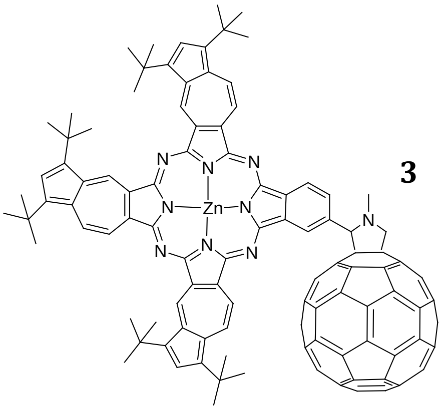


Figure S3. Upper part: MS spectrum for formyl-azulenocyanine **4**.

Lower part: A) experimental isotopic pattern and B) calculated isotopic pattern of $[M]^+$ peak of **4**.

Azulenocyanine-C_{60} dyad 3 (mixture of regioisomers)



3

A mixture of C_{60} (54.5 mg, 0.075 mmol), N-methylglycine (4.8 mg, 0.054 mmol) and azulenocyanine **4** (30 mg, 0.027 mmol) was heated under reflux overnight in dry toluene (60 mL) under argon atmosphere. After cooling to room temperature, the solvent was evaporated to dryness. Purification of the solid residue by column chromotography on silica gel (toluene followed by toluene/THF 10:1), and then size-exclusion column chromotograpy (Bio-Beads SX1, THF) gave pure azulenocyanine-C_{60} **3** (21 mg, 42%) as a black greyish solid.

^{1}H-NMR (d_8-THF, 300 MHz) δ (ppm): 11.5-11.0 (m, 3H, ArH), 9.8-9.2 (m, 8H, ArH), 8.3-8.2 (m, 4H, ArH), 5.5- 5.3 (m, 3H, pyrrolidine H), 3.34 (s, 3H, NCH_3), 2.0-1.4 (m, 54H, alkylH).

UV/Vis (THF): λ_{max} (nm) = 375, 500-1100 (broad).

FT-IR (film) ν (cm^{-1}): 2920, 2866, 1740, 1564, 1524, 1416, 1362, 1335, 1240, 1213, 1051, 957, 889, 768, 675.

MS (MALDI, dithranol), m/z: 1837.5 $[M]^+$. HRMS (MALDI-TOF, DCTB): calc. for $C_{131}H_{75}ZnN_9$: $[M]^+$: m/z: 1837.5431 found 1837.5394.

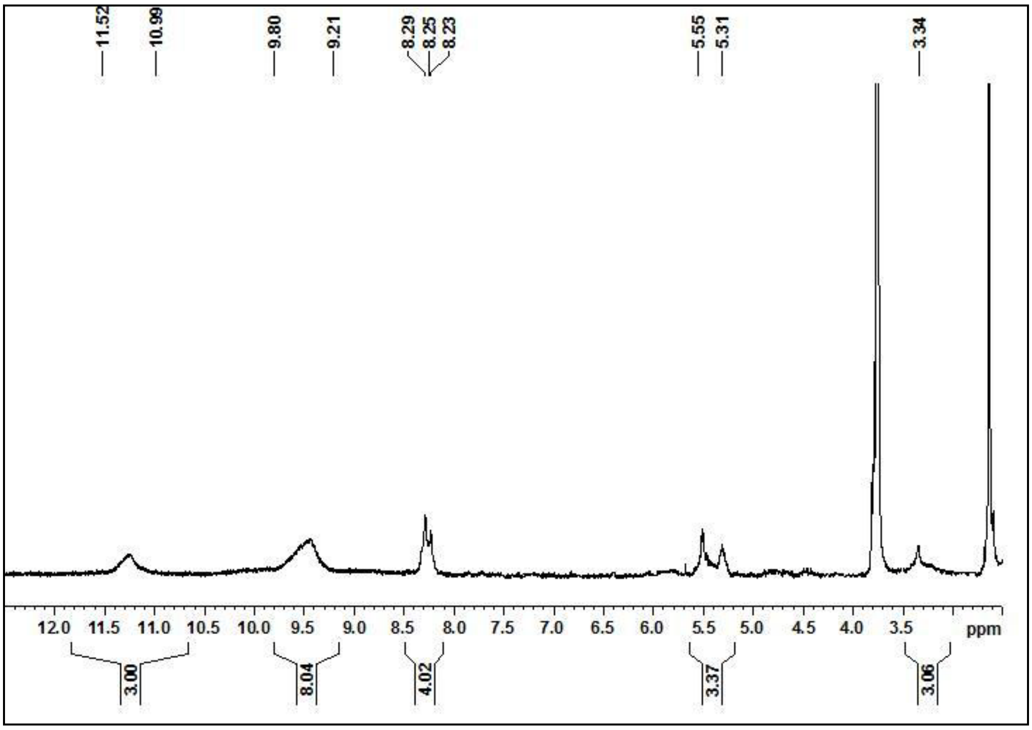


Figure S4. ^{1}**H**-NMR spectrum for Azulenocyanine-C_{60} dyad **3** in d_8-THF

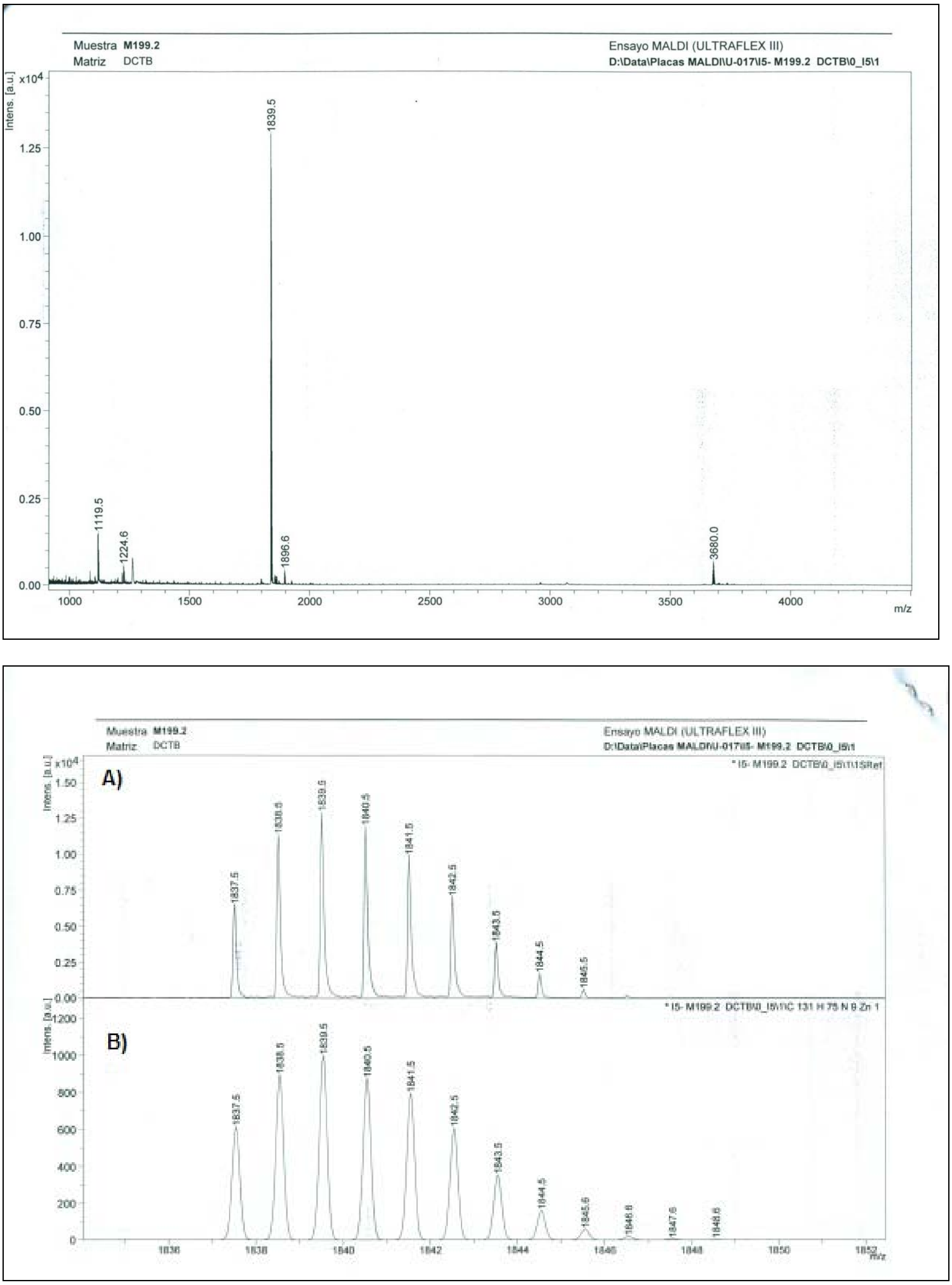


Figure S5. Upper part: MS spectrum for Azulenocyanine-C_{60} dyad **3.**

Lower part: A) Experimental isotopic pattern and B) calculated isotopic pattern of $[M]^+$ peak of **3**.

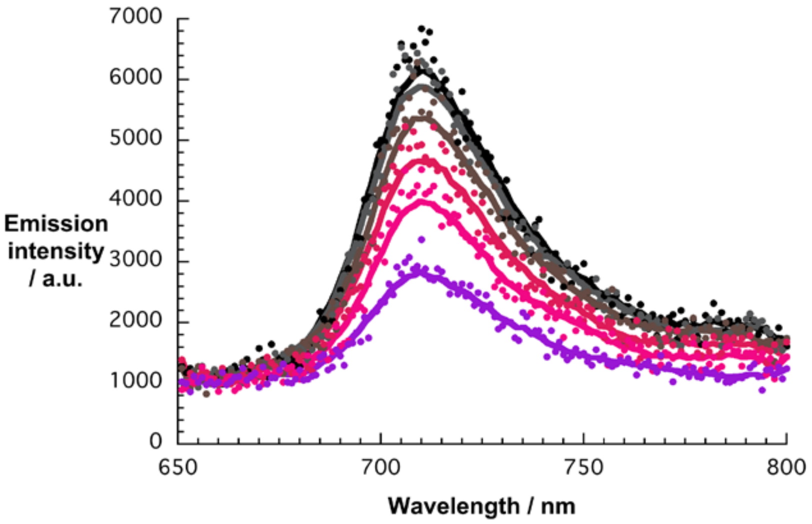
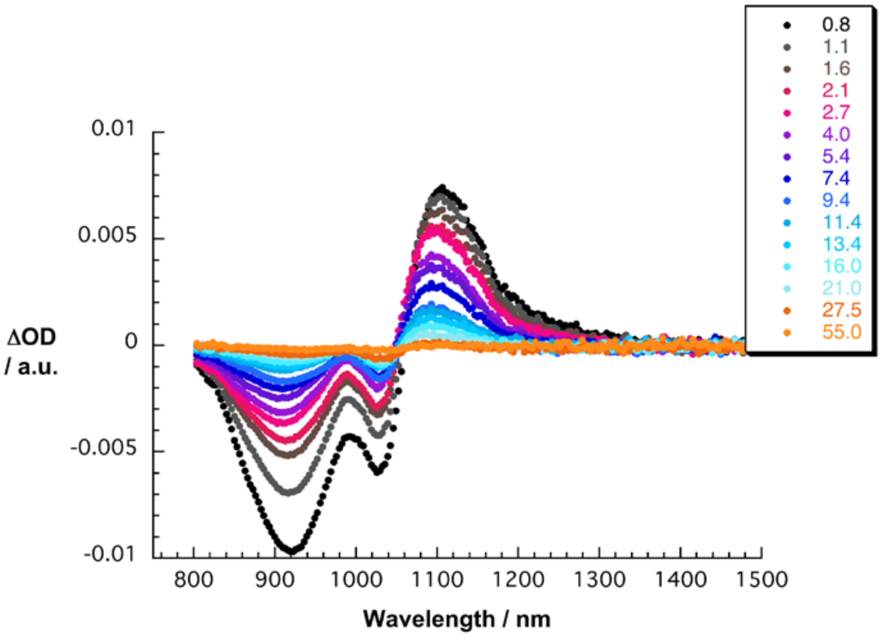


Figure S6. Room temperature fluorescence spectra of **1** (1.0×10^{-6} M) in chlorobenzene titrated with variable concentrations of **2** ($0 – 7.6 \times 10^{-6}$ M) at 500 nm excitation wavelength.



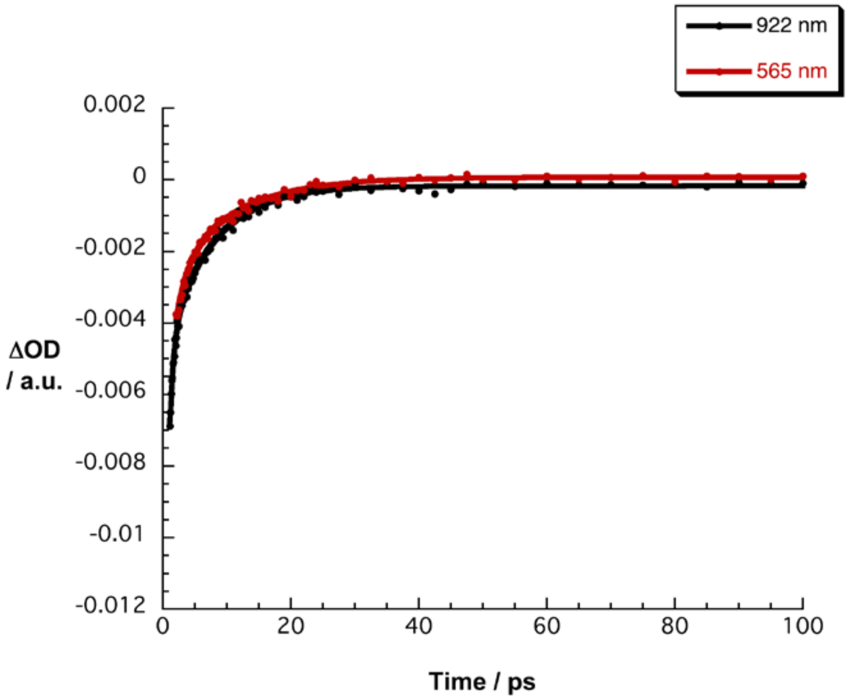


Figure S7. Differential absorption spectra (near-infrared) obtained upon femtosecond flash photolysis (387 nm) of an argon saturated THF solution of **3** at different time delays (between 0.8 and 55.0 ps) at room temperature. Bottom: Time profiles of the spectra shown above at 565 (red line) and 922 nm (black line).

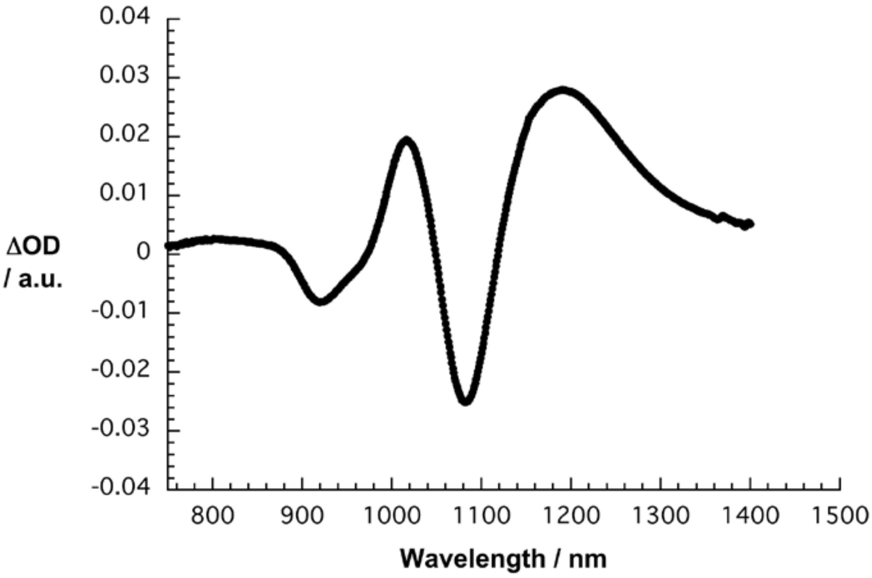


Figure S8. Spectroelectrochemical oxidation of **2** in dichloromethane at an applied potential of +0.25 V.

---

[1] Y. Lu, D. M. Lemal, J. P. Jasinski, *J. Am. Chem. Soc*. 2000, **122**, 2440.