Supporting Information

Bowl-shape Electron Donors with Absorptions in the Visible Range of the Solar Spectrum and their Supramolecular Assemblies with C_{60}

Helena Isla,[a] Bruno Grimm,[b] Emilio M. Pérez,[c] M. Rosario Torres,[a] M. Ángeles Herranz,[a] Rafael Viruela,[d] Juan Aragó,[d] Enrique Ortí,*[d] Dirk Guldi,*[b] Nazario Martín,*[ac]

[a] Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, E-28040 Madrid, Spain, [b] Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials (ICMM), Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, D-91058 Erlangen, Germany, [c]IMDEA-nanociencia, E-28049 Madrid, Spain, [d] Instituto de Ciencia Molecular, Universidad de Valencia, E-46980 Paterna, Spain

e-mail: enrique.orti@uv.es, guldi@chemie.uni-erlangen.de, nazmar@quim.ucm.es

1. Supporting figures:

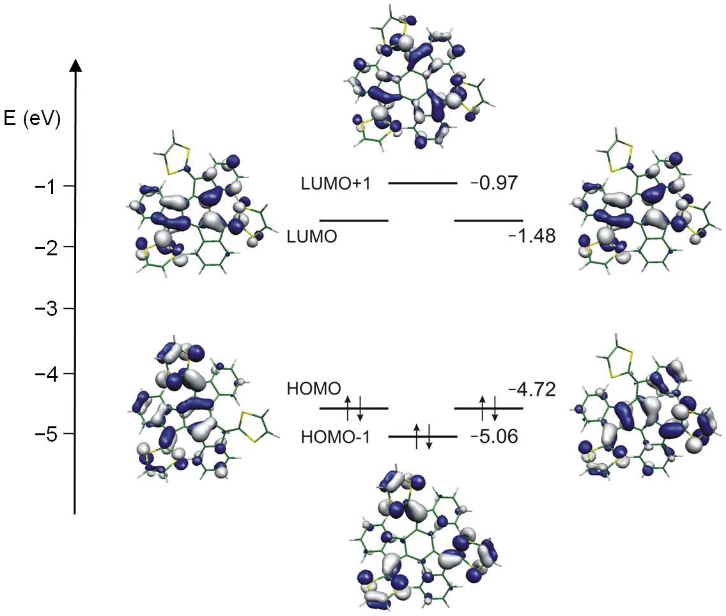


Figure S1. Electron density contours (0.03 e bohr^{-3}) and energies calculated for the HOMOs and LUMOs of **1** at the B3LYP/6-31G** level. Both the HOMO and the LUMO are doubly degenerate due to the C_3 symmetry of the molecule.

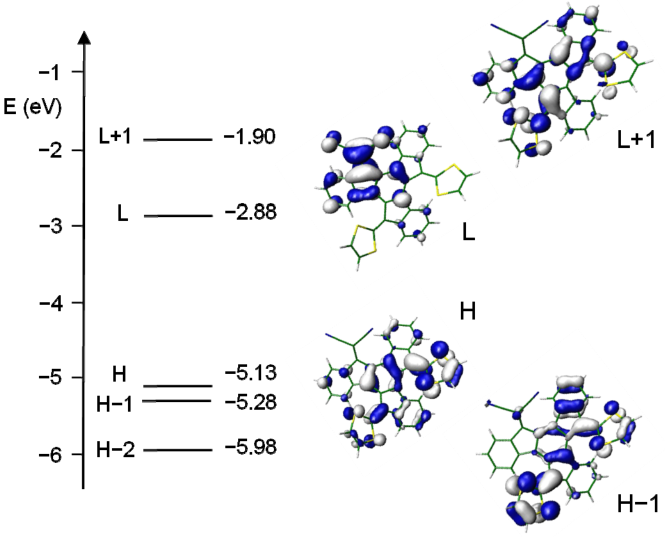


Figure S2. Electron density contours (0.03 e bohr^{-3}) and energies calculated for the HOMOs and LUMOs of **3** at the B3LYP/6-31G** level. H and L denote HOMO and LUMO, respectively.

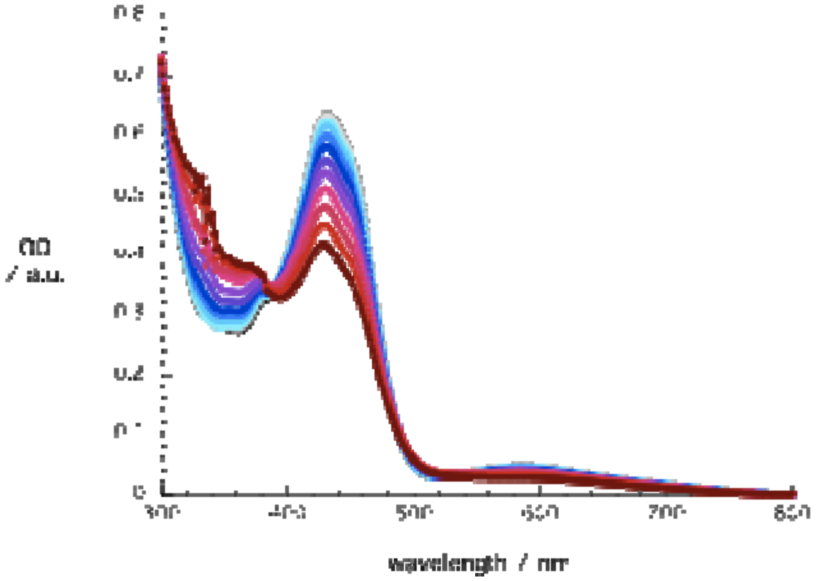


Figure S3 Absorption spectra of **3** (1.84 x 10^{-5}M) in toluene with variable concentrations of C_{60} (0; 2.96 x 10^{-6}M; 5.78 x 10^{-6}M; 8.47 x 10^{-6}M; 1.10 x 10^{-5}M; 1.58 x 10^{-5}M; 2.02 x 10^{-5}M; 2.62 x 10^{-5}M; 3.15 x 10^{-5}M; 3.77 x 10^{-5}M; 4.31 x 10^{-5}M and 5.20 x 10^{-5}M). C_{60} absorptions were subtracted.

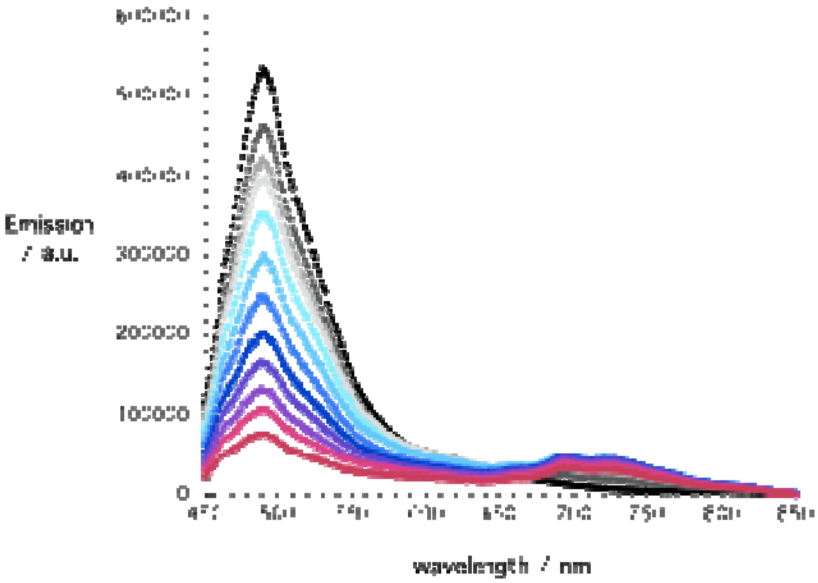
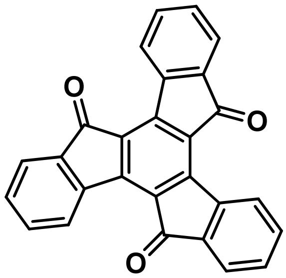


Figure S4 Emission spectra upon 350 nm excitation of a dilute toluene solution of **3** (1.84×10^{-5}M) with variable concentrations of C_{60} (0; 2.96×10^{-6}M; 5.78×10^{-6}M; 8.47×10^{-6}M; 1.10×10^{-5}M; 1.58×10^{-5}M; 2.02×10^{-5}M; 2.62×10^{-5}M; 3.15×10^{-5}M; 3.77×10^{-5}M; 4.31×10^{-5}M and 5.20×10^{-5}M).

2. Synthesis and characterization

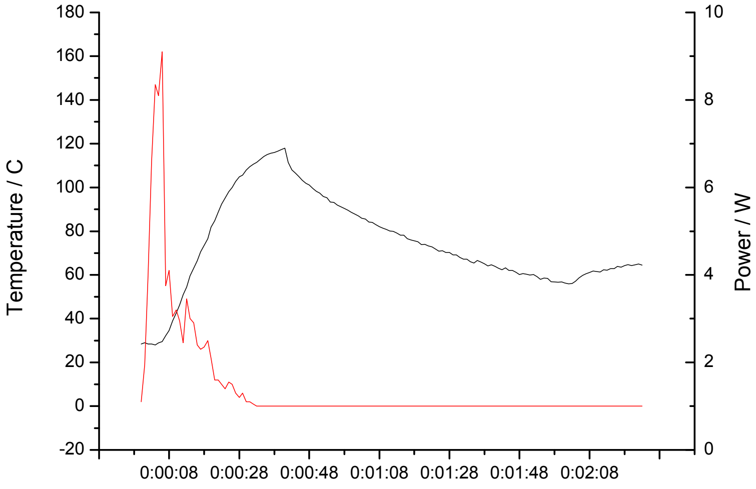
General. All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh, or Scharlau 60, 230-240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminium-coated Merck Kieselgel 60 F254 plates. Melting points were determined on a Gallenkamp apparatus. NMR spectra were recorded on a Bruker Avance 300 (^{1}H: 300 MHz; ^{13}C: 75 MHz) a Bruker Avance 500 (^{1}H: 500 MHz; ^{13}C: 125 MHz) or a Bruker AvanceIII 700 (^{1}H: 700 MHz; ^{13}C 175 MHz) spectrometers at 298 K, unless otherwise stated, using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. Electrospray ionization mass spectra (ESI-MS) and Matrix assisted Laser desorption ionization (coupled to a Time-of-Flight analyzer) experiments (MALDI-TOF) were recorded on a HP1100MSD spectrometer and a Bruker REFLEX spectrometer, respectively. UV/Vis spectra were recorded with Varian Cary 50. Steady state fluorescence studies were carried out on a Fluoromax 3 (Horiba) instrument and all the spectra were corrected for the instrument response. The femtosecond transient absorption studies were performed with laser pulses (1Khz 150 fs pulse width) from an amplified Ti:Sapphire laser system (Model CPA 2101, Clark-MXR Inc.). Mass spectra were recorded with a HP 5989A spectrometer. Cyclic voltammograms were acquired using a three-electrode cell equipped with a glassy carbon working electrode (Ø = 3 mm), a platinum wire as a counter-electrode, an Ag/AgNO$_3$ reference on an Autolab potentiostat. Before the acquisition, solutions were systematically degassed by bubbling argon for five minutes.



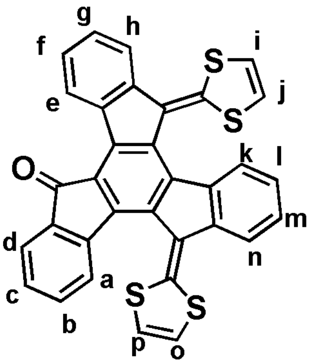
Chemical Formula: $C_{27}H_{12}O_3$

Molecular Weight: 384.38

1.0g of 1,3 indandione (6.8 mmol) were dissolved in 16 mL of methanesulfonic acid, and the solution placed in an standard microwave 30 mL vial equipped with a magnetic stirrer bar. This solution was heated to 110 ºC in an Anton Paar Monowave 300 microwave synthesis reactor utilizing the “as fast as possible” heating mode with stirring, and a hold temperature time of 5 seconds. The resulting suspension was poured into 10 mL of water and filtered. The solid was successively washed with copious amounts of water and methanol, then recrystallized from propylene carbonate and from picoline, and finally washed with diethyl ether and dried, to obtain 0.675 g (1.7 mmol, y = 77 %) of truxenone. This compound showed identical analytical and spectroscopic data to those reported in L. Sanguinet, J. C. Williams, Z. Yang, R. J. Twieg, G. Mao, K. D. Singer, G. Wiggers and R. G. Petschek, *Chem. Mater.*, 2006, **18**, 4259.



Anton Paar Monowave - Processing Protocol (Serial Number: 80571612)

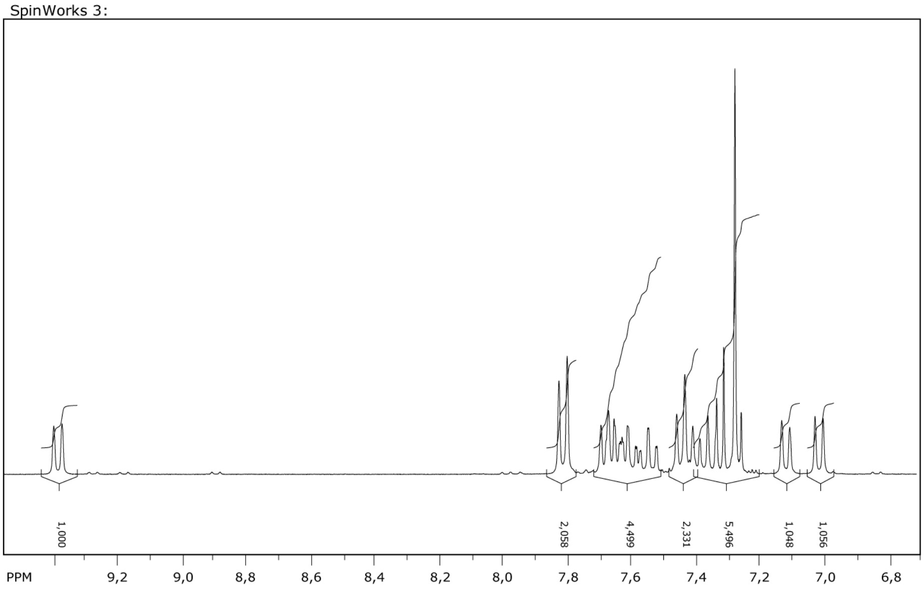


Chemical Formula: $C_{33}H_{16}OS_4$

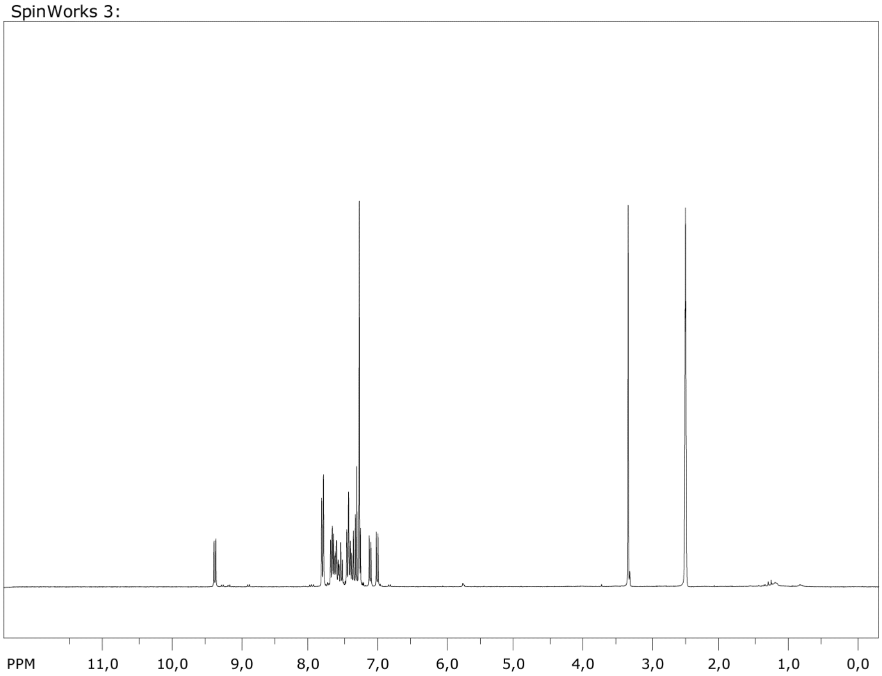
Molecular Weight: 556.74

A solution of dimethyl 1,3-dithiol-2-ylphosphonate 1.10 g (5.2 mmol) in 10 mL of dry THF was cooled to –78 ºC, and then BuLi (2.6 mL, 2 M in hexane, 5.2 mmol) was added. The solution was left to stir at –78 ºC for 15-20 min, with appearance of a yellow precipitate. In the meantime, a suspension of 1.0 g of the truxenone precursor (2.6 mmol) in 30 mL of dry THF was dispersed with sonication for *ca.* 30 min. The resulting suspension was added to the phosphorous ylide suspension, and the cooling bath immediately removed. The mixture was allowed to warm to room temperature and left to stir for 2 h. The solvent was taken up and the residue was purified by column chromatography (SiO_2, Hexane: Dichloromethane 2:1). After purification 0.54 g (y = 37%) of the pure product was obtained as a black solid.

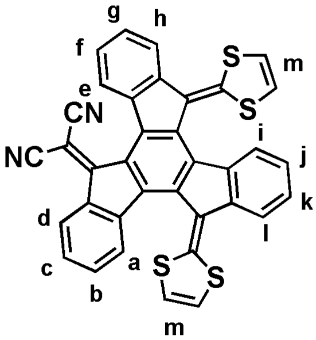
Mp. > 300 ºC; ^{1}H NMR (DMSO) δ 9.39 (1H, d, J = 7.6 Hz, a), 7.81 (2H, d, J = 7.6 Hz, e + k), 7,70-7.51 (4H, m, f + g + l + m), 7.45 (2H, t, J = 7.6 Hz, b + c), 7.39-7.25 (5H, m, i + j + o + p + h/n), 7.12 (1H, d, J = 7.6 Hz, d), 7.04 (1H, d, J = 7.6 Hz, h/n) ppm. ^{13}C NMR (DMSO) δ 194.2, 146.1, 144.2, 144.0, 142.3, 141.7, 136.8, 135.9, 135.7, 135.2, 135.0, 134.9, 134.8, 133.5, 133.3, 129.8, 128.9, 128.5, 128.4, 127.9, 127.3, 126.7, 126.1, 125.4, 124.1, 123.7, 123.5, 122.6, 122.5, 121.0, 120.2, 120.1 ppm. MS-ESI (neg.) m/z 554.8 [M-H$^+$]. HRMS calcd. for $C_{33}H_{16}NaOS_4$ [M+Na$^+$] = 578.99762; found (ESI pos.) 579.00065. IR = 3068, 2923, 2854, 1698, 1602, 1570, 1541, 1494, 747 cm^{-1}. UV (CH_2Cl_2, 298 K) λ_{max} (log ε): 274.06 (4.64), 402.02 (4.46), 537.02 nm (3.67).



```
file: F:\RMN\Q07HI12DMSO\3\fid   expt: <zg30>                    freq. of 0 ppm: 300,130002 MHz
transmitter freq.: 300,131501 MHz                                processed size: 32768 complex points
time domain size: 16384 points                                   LB: 0,000    GF: 0,0000
width: 4496,40 Hz = 14,9814 ppm = 0,274439 Hz/pt                 Hz/cm: 34,231    ppm/cm: 0,11405
number of scans: 16
```



```
file: ...\RMN(pre-laptop)\Q07HI12DMSO\3\fid   expt: <zg30>        freq. of 0 ppm: 300,130002 MHz
transmitter freq.: 300,131501 MHz                                processed size: 32768 complex points
time domain size: 16384 points                                   LB: 0,000    GF: 0,0000
width: 4496,40 Hz = 14,9814 ppm = 0,274439 Hz/pt                 Hz/cm: 179,856    ppm/cm: 0,59926
number of scans: 16
```

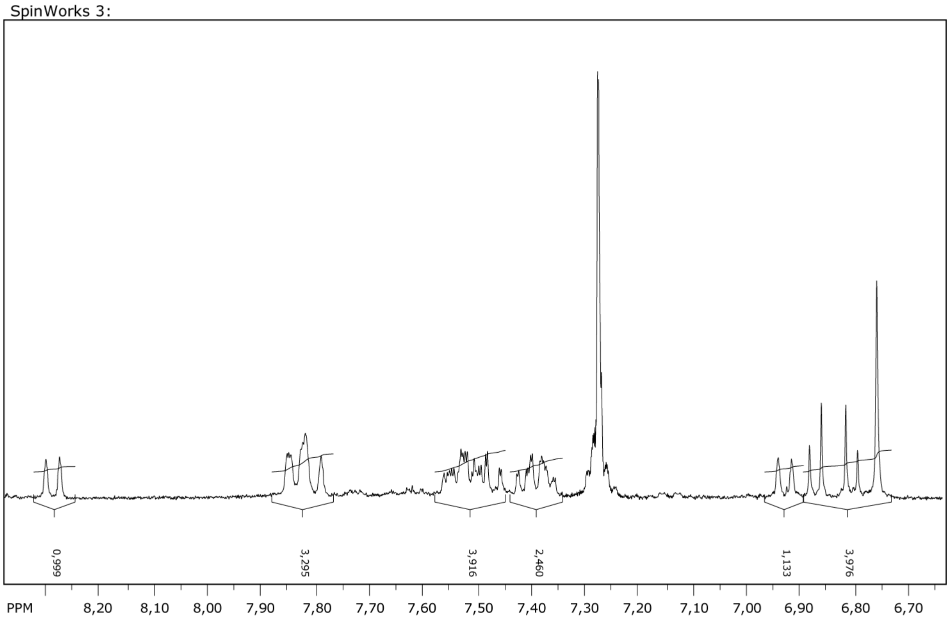


Chemical Formula: $C_{36}H_{16}N2S4$

Molecular Weight: 604.79

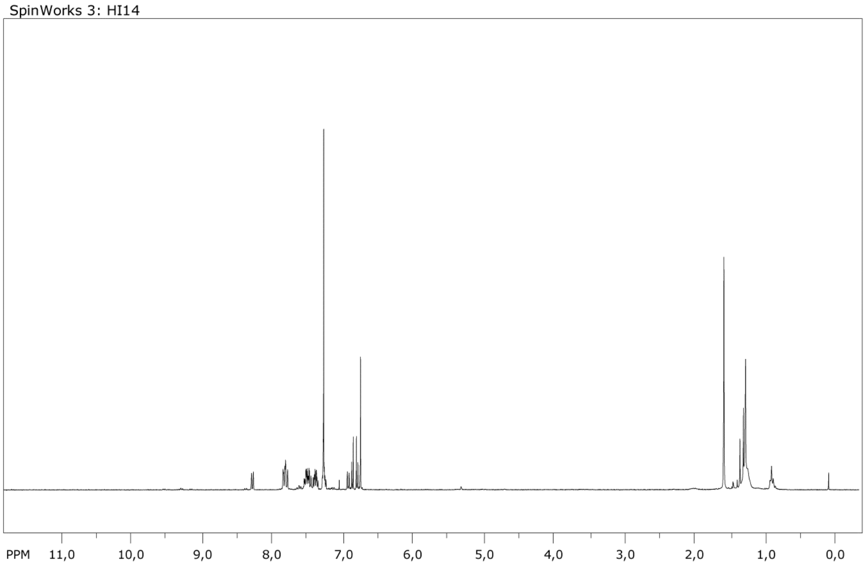
A mixture of 25 mg of **2** (0.045 mmol) and 8.9 mg (0.135 mmol) of malononitrile in 15 mL of chlorobenzene was treated by ultrasound irradiation for 30 minutes. Then 0.015 mL of $TiCl_4$ (0.135 mmol) and 0.02 mL of pyridine (0.225 mmol) were added successively. The reaction mixture was stirred at room temperature for 2 hours. The solvent was removed under vacuum and the crude purified by column chromatography (SiO_2 Hexane:Dichloromethane 2:1). After purification 7.5 mg (y = 28%) of pure product was obtained as deep green solid. 10 mg (y = 40%) of pure **2** were also recovered.

Mp. > 300 ºC; ^{1}H NMR($CDCl_3$) δ 8.28 (1H, d, J = 8.2 Hz, a); 7.86-7.77 (3H, m, e + h + l); 7.52 (1H, td, J = 7.6 y 1.2 Hz, f /g); 7.51 (1H, td , J = 7.6 y 1.2 Hz, f/g); 7.46 (1H, dd, J = 7.6 y 1.0 Hz, d); 7.39 (1H, td, J = 7.7 y 1.1 Hz, j/k); 7.38 (1H, td, J = 7.7 y 1.1 Hz, j/k); 7.30-7.23 (2H, m, b + c); 6.92 (1H, bd, J = 7.7 Hz, i); 6.88- 6.73 (4H, m, m) ppm. ^{13}CRMN ($CDCl_3$) δ: 142.7, 142.3, 142.2, 141.6, 137.8, 135.8, 135.3, 133.0, 129.3, 128.7, 128.0, 127.8, 127.3, 125.5, 125.1, 124.8, 123.0, 122.3, 121.8, 119.1, 119.0, 114.8 ppm. MS-ESI m/z= 627.0 [$M+Na^+$]. HRMS calcd. for $C_{36}H_{16}N_2NaS_4$ [$M+Na^+$] = 627.00885 found (ESI pos.) 627.01189. IR = 2923, 2852, 2222(υ_{CN}), 1596, 1541, 1499, 1464, 769 cm^{-1}. UV–Vis (CH_2Cl_2, 298 K) λ_{max} (log ε): 430.97 (4.48), 594.02 nm (3.38).



file: F:\RMN\Q07HI14\1\fid   expt: <zg30>
transmitter freq.: 300,131501 MHz
time domain size: 16384 points
width: 4496,40 Hz = 14,9814 ppm = 0,274439 Hz/pt
number of scans: 16

freq. of 0 ppm: 300,130002 MHz
processed size: 32768 complex points
LB: 0,000   GF: 0,0000
Hz/cm: 20,980   ppm/cm: 0,06990



file: ...\RMN\RMN(pre-laptop)\q07HI55\1\fid   expt: <zg30>
transmitter freq.: 300,131501 MHz
time domain size: 16384 points
width: 4496,40 Hz = 14,9814 ppm = 0,274439 Hz/pt
number of scans: 16

freq. of 0 ppm: 300,130002 MHz
processed size: 32768 complex points
LB: 0,000   GF: 0,0000
Hz/cm: 146,195   ppm/cm: 0,48710

Crystallographic Data:

The structure was solved by direct methods and refined by full-matrix least-square procedures on F^2 (SHELXL-97, G.M. Sheldrick, ‘SHELXTL’ ver. 6.12 , Program for Refinement of Crystal Structure’, University of Göttingen, Göttingen, Germany, 1997). All non-hydrogen atoms were refined anisotropically.

The hydrogen atoms were included in their calculated positions and refined riding on the respective carbon atoms. After refining, the presence of solvent residual electron density was detected as disordered atomic groups located in the void regions, and centered in sites among the molecule. The solvent molecule could not be modeled properly in none of the crystals, due to the poor spectra quality. The program SQUEEZE, a part of the PLATON (A.L. Speck, PLATON, Utrecht University, Utrecht, The Netherlands, 2005) package of crystallographic software, was used to calculate the solvent disordered area and remove its contribution to the overall intensity data. An improvement was observed in all refinement parameters and residuals when this procedure was applied.

Table S1. Crystal data and structure refinement for C33H16O1S4.

Empirical formula	C33 H16 O S4	
Formula weight	556.70	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.030(5) Å	α= 112.013(6)°.
	b = 12.159(5) Å	β= 104.449(7)°.
	c = 12.875(6) Å	γ = 96.026(8)°.
Volume	1511.7(11) Å^3	
Z	2	
Density (calculated)	1.223 Mg/m^3	
Absorption coefficient	0.337 mm^{-1}	
Independent reflections	5188 [R(int) = 0.1357]	
Final R indices [I>2sigma(I)]	R1 = 0.0744, wR2 = 0.1152	

$R1=\sum | |Fo| - |Fc| | / \sum |Fo|$
$wR2= \{\sum[w(Fo^2-Fc^2)^2]/\sum[w(Fo^2)^2]\}^{1/2}$

Theoretical Calculations. Theoretical calculations were carried out within the density functional theory (DFT) approach by using the A.02 revision of the Gaussian 09 program package.[1] Geometry optimizations of compounds **1–3** were performed with Becke's three-parameter B3LYP exchange functional[2] and the 6-31G** basis set.[3] Dications were calculated both as singlet-state closed-shell species and as triplet-state open-shell species using for the latter spin-unrestricted UB3LYP wave functions. Open-shell anions were also computed using the UB3LYP approach. Molecular orbitals were plotted using Molekel 4.3.[4] Vertical electronic transition energies to the lowest-energy 50 excited states were computed at the B3LYP/6-31G** level using the time-dependent DFT (TDDFT) approach and the optimized ground-state molecular geometries. The vertical excitation energies were also calculated using the hybrid PBE0 functional.[5] The PBE0 functional led to slightly higher energies (~0.1 eV) for the excited states and to an identical description of the electronic spectra. TDDFT calculations were also performed in the presence of the solvent to study the influence of solvent polarity on the electronic absorption spectrum. Solvent effects were considered within the SCRF (self-consistent reaction field) theory using the polarized continuum model (PCM)[6] approach to model the interaction with the solvent. The PCM model considers the solvent as a continuous medium with a dielectric constant ε, and represents the solute by means of a cavity built with a number of interlaced spheres.[7] The solvents considered were CH_2Cl_2 ($\varepsilon = 8.93$) and CH_3CN ($\varepsilon = 36.64$). TDDFT calculations in the presence of the solvent led to a description of the electronic absorption spectra identical to that obtained for the isolated molecule and confirm the charge transfer nature of the S_1 and S_2 excited states.

Calculations on supramolecular complexes of compounds **1–3** with C_{60} were performed making use of Becke's "half-and-half" (BH&H) functional[8] and of the hybrid meta M06-2X functional developed by Truhlar et al.[9] The BH&H functional is an *ad hoc* mixture of exact Hartree-Fock (HF) and local density approximation (LDA) exchange, coupled with Lee, Yang, and Parr's (LYP) expression[10] for the correlation energy. It has been found to provide binding energies for the archetypal parallel-displaced benzene dimer in good agreement with the best available high-level computational methods,[11] and to show good performance for dispersion-dominated systems.[12] The M06-2X functional has been especially designed to deal with noncovalent interactions. The B3LYP functional was not employed to calculate the supramolecular complexes because it fails in describing dispersion forces and does not properly account for stacking π-π interactions.[13]

Association binding energies were firstly obtained at the BH&H/6-31G** and M06-2X/6-31G** levels by fully optimizing the geometry (intra- and intermolecular parameters) of the supramolecular complex. Binding energies were afterwards recalculated using the more extended cc-pVTZ basis set,[14] and the 6-31G**-optimized geometries. The basis set superposition error (BSSE) was computed using the counterpoise correction approach.[15] The BSSE is a spurious contribution to the interaction energy arising from the improved description of the molecular fragment A in the complex A•••B due to the assistance of the basis set located in fragment B, and vice versa. The counterpoise method corrects the interaction energy of the complex A•••B by computing the energies of the isolated fragments A and B with exactly the same basis set (both in number and location) as used to compute the complex A•••B.

The association binding energies were also calculated at the M06-2X/6-31G** level in the presence of the solvent (toluene) using the PCM approach and fully reoptimizing the geometry of the supramolecular complex. The solvent reduces the binding energies calculated for complexes $\mathbf{1}\cdot C_{60}$, $\mathbf{2}\cdot C_{60}$, and $\mathbf{3}\cdot C_{60}$ to –8.71, –6.76, and –7.98 kcal mol^{-1}, respectively, thus preserving the relative stability predicted in gas phase (–17.73, –15.32, and –17.15 kcal mol^{-1}, respectively). Therefore, the theoretical ordering predicted for the association binding energy ($\mathbf{1}\cdot C_{60} > \mathbf{3}\cdot C_{60} > \mathbf{2}\cdot C_{60}$) do not reproduce the experimental ordering deduced from absorption and fluorescence data for the binding constant ($\mathbf{1}\cdot C_{60} > \mathbf{2}\cdot C_{60} > \mathbf{3}\cdot C_{60}$.). The main limitation of the PCM approach is that it defines the solvent as a continuum polar medium and does not take properly into account the discrete interactions between the solvent and the solute molecules. A more elaborated model is therefore needed to correctly describe the formation of the supramolecular complexes in the presence of the solvent.

References

(1) Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark,V; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian, Inc., Wallingford CT, 2009.

(2) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(3) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Defrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(4) Flukiger, P.; Lüthi, H. P.; Portmann, S.; Weber, J., MOLEKEL 4.3; Swiss Center for Scientific Computing, Manno, Switzerland, **2002** (htpp://www.cscs.ch/molekel/). Portmann, S.; Lüthi, H. P. *Chimia* **2000**, *54*, 766.

(5) Ernzerhof, M.; Scuseria, G. E. *J. Chem. Phys.* **1999**, *110*, 5029. Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.

(6) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027. Cramer, C. S.; Truhlar, D. G. *Solvent Effects and Chemical Reactivity*, Kluwer, Dordrecht, **1996,** pp 1–80.

(7) Miertus, S.; Scrocco, E.; Tomasi, J.; *Chem. Phys.* **1981**, *55*, 117. Miertus, S.; Tomasi, J. *J. Chem. Phys.* **1982**, *65*, 239. Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys. Lett.* **1996**, *255*, 327. Cances, E.; Mennucci, B.; Tomasi, J. *J. Chem. Phys*., **1997**, *107*, 3032. Barone, V.; Cossi, M.; Tomasi, J. *J. Comput Chem*. **1998**, *19*, 404. Cossi, M.; Scalmani, G.; Rega, N.; Barone, V. *J. Chem. Phys.* **2002**, *117*, 43.

(8) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

(9) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.

(10) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(11) Waller, M. P.; Robertazzi, A.; Platts, J. A.; Hibbs, D. E.; Williams, P. A. *J. Comput. Chem.* **2006**, *27*, 491. Robertazzi, A.; Platts, J. A. *J. Phys. Chem. A*, **2006**, *110*, 3992.

(12) Zhao, Y.; Truhlar, D. G. *J. Chem. Theory Comput.* **2007**, *3*, 289. Valdes, H.; Pluháčková, K.; Pitonák, M.; Řezáč, J.; Hobza, P. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2747. Gkionis, K.; Hill, J. G.; Oldfield, S. P.; Platts, J. A. *J. Mol. Model.* **2009**, *15*, 1501.

(13) Tsuzuki, S.; J. Luthi, H. P. *Chem. Phys.* **2001**, *114*, 3949. Zhao, Y.; J. Truhlar, D. G. *J. Chem. Theory Comput.* **2005**, *1*, 415.

(14) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(15) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.