Supplementary material (ESI) for Journal of Materials Chemistry

Functionalised 9-(1,3-dithiol-2-ylidene)thioxanthene derivatives: a C_{60} conjugate as an ambipolar organic field effect transistor (OFET)

Electronic Supplementary Information

Characterisation Data for Compound 6:

Dark brown solid, mp 181-183 °C*,* *m/z* (MALDI) 1164.3 (M^+); ^{1}H NMR ($CDCl_3$): δ (ppm) 8.63 (d, 2H, *J*=8 Hz), 7.62 (m, 6H), 7.50 (t, 3H, *J*=4 Hz, *J*=6 Hz), 7.42 (d, 1H, *J*=4 Hz), 5.00 (t, 2H, *J*=4 Hz), 4.29 (d, 1H, *J*=8 Hz), 2.83 (s, 3H, *NCH_3*), 2.18 (s, 3H, *CH_3*). ^{13}C NMR ($CDCl_3$): δ 180.2, 147.6, 146.8, 146.62, 146.56, 146.48, 146.38, 146.2, 146.1, 146.0, 145.8, 145.6, 145.54, 145.49, 145.0, 144.8, 144.7, 144.6, 143.4, 143.3, 143.0, 142.9, 142.5, 142.4, 142.3, 142.2, 142.13, 142.06, 141.95, 141.8, 140.5, 140.2, 139.6, 137.5, 132.5, 130.1, 129.5, 126.6, 126.2, 83.3, 70.3, 68.9, 40.3, 30.2, 15.6. UV/Vis ($CHCl_3$): λ_{max} (lg ε) 374 (0.62), 433 (0.13), 704 (0.004), 874 (0.02), 909 (0.008) nm. IR (KBr) 2922, 2788, 2372, 2348, 1653, 1640, 1596, 1507, 1458, 1324, 736, 669, 526 cm^{-1}. The absorption band at λ_{max} 374 nm is derived from the donor unit; the diagnostic features of C_{60} derivatives possessing a saturated 6,6-bond are the sharp peak at λ_{max} 433 nm and a broad band at λ_{max} 704 nm.

OFET Device Fabrication.

A standard top-contact FET device configuration was used. A layer of SiO_2 (50 nm) was grown on top of heavily-doped silicon (100) wafers. Compound **6** was spin-coated from *o*-dichlorobenzene solution to give a 100 nm thick film. Gold source and drain electrodes were then vapour deposited through a shadow mask, with a channel length and width of 20μm and 1.0 mm, respectively. Current-voltage characteristics were measured under vacuum (*ca*. 20 mTorr) at room temperature.

Theoretical calculations.

The geometry optimisation of compound **6** was performed by semi-empirical PM3 methods implemented into Hyperchem modelling software (Figure S1).[1]
The electronic structure was calculated at the DFT level, as a single point calculation for UPM3 optimised geometry using the Gaussian 98 package of programs.[2] DFT calculations were carried out using Becke's three-parameter hybrid exchange functional[3] with Lee–Yang–Parr gradient-corrected correlation functional (B3LYP).[4] Pople's 6-31G split valence basis set supplemented by *d*-polarisation functions on heavy atoms was used. Unrestricted HF formalism was applied at both geometry optimization and single point calculation of the electronic structure. Contours of HOMO and LUMO orbitals have been visualised using the Molekel v.4.3 program.[5]

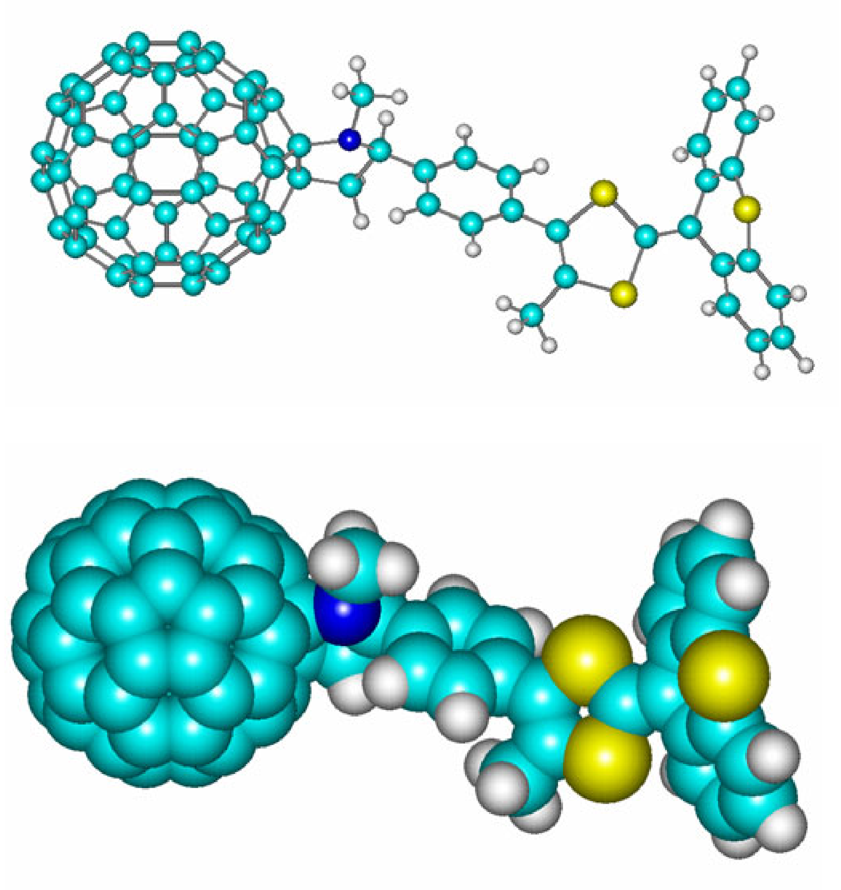
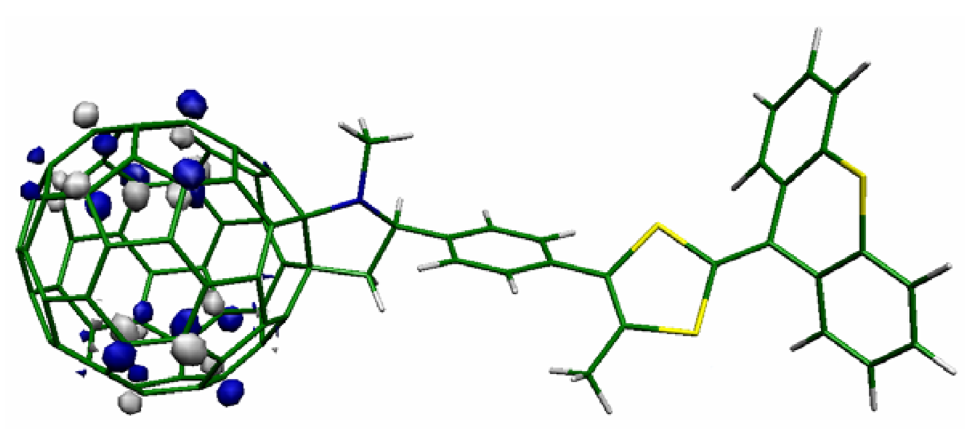
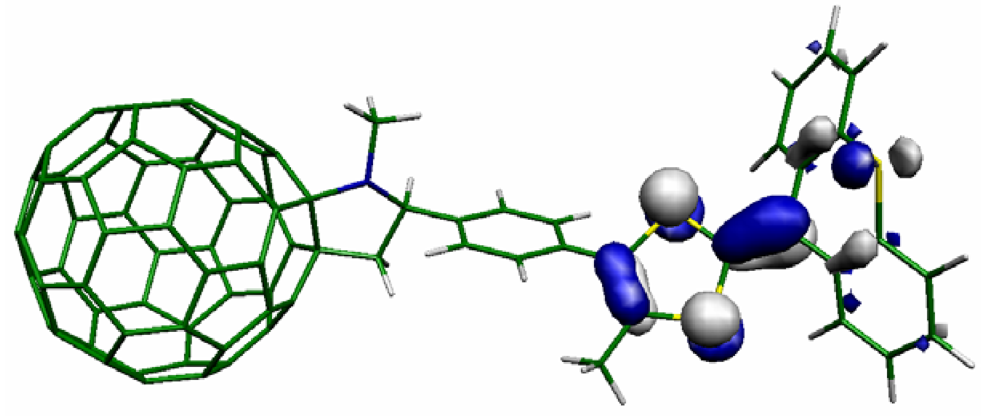


Figure S1. UPM3 optimised geometry of compound **6** (calculated length ca. 23 Å).



$E_{\mathrm{LUMO}} = -3.17$ eV



$E_{\mathrm{HOMO}} = –4.69$ eV

Figure S2. LOMO (top) and HOMO (bottom) orbital localisation in molecule **6** according to UB3LYP/6-31G(d)//UPM3 calculations ($\Delta E_{\mathrm{HOMO–LUMO}} = 1.52$ eV = 815 nm).

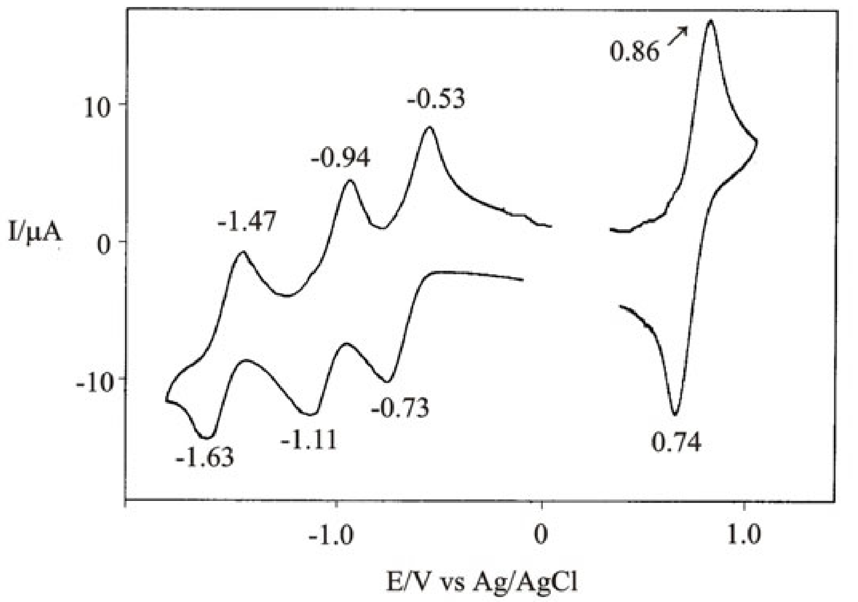


Fig S3. Cyclic voltammogram of compound **6**. For conditions, see Table 1.

References

1. HyperChem™ Molecular Modelling System, Release 6.03 for Windows. Hypercube, Inc. 2000.
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3. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
4. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

5. (a) P. Flükiger, H. P. Lüthi, S. Portmann, J. Weber, Molekel, Version 4, Swiss Center for Scientific Computing, Manno (Switzerland), 2000. S. Portman, Molekel, Version 4.3.win32, CSCS/ETHZ, 2002; http://www.cscs.ch/molekel/; (b) S. Portmann, H. P. Lüthi, *Chimia*, 2000, **54**, 766.