

Synthesis and photoresponse of a fullerene–bis(styryl)benzene dyad†

Nadia Camaioni,^{*b} Graziano Fabbri,^a Enzo Menna,^a Michele Maggini,^{*a}
Giovanni Ridolfi^b and Alberto Zanelli^b

Received (in Montpellier, France) 16th December 2005, Accepted 24th January 2006

First published as an Advance Article on the web 9th February 2006

DOI: 10.1039/b517933e

As part of our investigations into single-component organic solar cells, a symmetrical bis(styryl)benzene–fullerene dyad has been synthesized. An oxyethylene macrocyclic spacer, attached to *meta*-positions of side phenyl groups of bis(styryl)benzene, was linked to [60]fullerene through a synthesis based on the nucleophilic Bingel cyclopropanation of the fullerenes. The dyad structure was confirmed by ¹H, ¹³C and HR-FAB mass spectra. The UV-Vis spectrum of the dyad is the superimposition of those of appropriate model systems, indicating that ground-state electronic interactions between the constituent chromophores, in solution, are negligible, in line also with the electrochemical results. Molecular modelling studies and NMR data suggest that the bis(styryl)benzene moves back and forth at room temperature from one side of the fullerene to the other. Interestingly, the overall power conversion efficiency (η) calculated for solar cells made of the bis(styryl)benzene–fullerene dyad was 0.022% under a white-light irradiation power of 86 mW cm^{−2}. This is, to our knowledge, the highest value reported, under high-level irradiation conditions, for solar cells based on dyads in which a fullerene is tethered to a phenylenevinylene structure.

1. Introduction

Plastic solar cells, made of an interpenetrating, bicontinuous network¹ of an electron donor conjugated polymer (D) and an electron acceptor functionalized fullerene (A) have shown potential to harness solar energy effectively², although low efficiency still limits their viability for commercial uses.³ However, following the fast growth of research in organic materials for solar energy conversion,⁴ key bottleneck factors to high-efficiency, such as photon losses, exciton losses or charge carrier mobility,³ especially that of the holes in donor polymers,⁵ have become clear. Efforts are therefore made to minimize these losses through the realization of nano-structured heterojunctions⁶ by controlling, for instance, the self-organization of the D/A components.⁷ Currently, the best conjugated polymer-based solar cells, reported in the literature, are those obtained by mixing poly(3-hexyl)thiophene and a soluble functionalized fullerene that gave a power conversion efficiency approaching 5% under standard test conditions.^{7c}

Alternative approaches to fullerene–polymer blends have been actively pursued as well by several groups.⁸ In the so-called *double cable* approach,⁹ for instance, functionalized fullerenes (n-cable) are tethered to a conjugated polymer

backbone (p-cable). The covalent grafting of the active components of the solar cell would prevent, at least in principle, either extensive phase segregation¹⁰ or unwanted ground state electronic interactions between D and A chromophores. Both electropolymerized¹¹ and solution processable^{11b,12} conjugated polymers with pendant fullerenes have been prepared and, in a few cases, tested in photovoltaic devices. Power conversion efficiency values of about 0.1%, under white light illumination of 100 mW cm^{−2} intensity, were reported for a methanofullerene covalently linked to a copolymer made of poly(*p*-phenylene)vinylene and poly(*p*-phenylene)ethynylene.^{12a} The optimization of the fullerene mole fraction remains, most likely, the major challenge for the development of efficient *double cable*, fullerene-based solar cells.⁹ It has been reported that a fullerene content as high as 80 wt% would ensure best performance for poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene]vinylene (MDMO-PPV)–fullerene derivative solar cells.¹³ More recently, it has been found that a 1:1 wt:wt fullerene–polymer ratio in the active layer yielded balanced electron and hole transport in cells where poly(3-hexylthiophene) was the donor.^{7b} To our knowledge, no soluble *double cable* materials, having such a large concentration of fullerene, have been reported yet.

Other promising approaches to plastic solar cells followed the considerable development of the chemistry of the fullerenes.¹⁴ They include the use of molecular dyads and triads made of a functionalized fullerene covalently linked to oligomeric, conjugated architectures that showed power conversion efficiencies ranging from about 10^{−2}% to our reported 0.37%, under 80 mW cm^{−2} white light illumination, for a fullerene–azothiophene dyad.¹⁵ In this connection, the first example of a single-component solar cell based on a fullerene–

^a Dipartimento di Scienze Chimiche and CNR-ITM, Università di Padova, via Marzolo 1, 35131 Padova, Italy. E-mail: michele.maggini@unipd.it; Fax: +39-049-8275792; Tel: +39-049-8275662

^b Istituto per la Sintesi Organica e la Fotoreattività (CNR-ISOF), via P. Gobetti 101, 40129 Bologna, Italy. E-mail: camaioni@isof.cnr.it; Fax: +39-051-6399844; Tel: +39-051-6399779

† Electronic supplementary information (ESI) available: HPLC analysis, ¹H NMR, ¹³C NMR and FAB mass spectra of dyad 1. See DOI: 10.1039/b517933e

bis(styryl)benzene conjugate was reported in 1999 by J.-F. Nierengarten and co-workers.¹⁶ Recently, accounts have been published¹⁷ in which sections are devoted to some aspects of this subject.

Several groups reported the synthesis and photophysical properties of triad ensembles.¹⁸ Also, a wide variety of other donor-linked fullerenes have been proposed in which the donor moiety is, for instance, a functionalized oligo(phenylene)vinylene,^{16,19} a Zn-phthalocyanine,²⁰ a dihexyloxybenzene-thiophene structure,²¹ a functionalized oligo(phenylene)ethynylene²² or an azaromatic dye.^{15,23} It is worth mentioning that a general phenomenon in fullerene-based D–A dyads is the competition between energy and electron transfer.^{18a,19a,24} This issue can be tackled by designing D–A molecular systems characterized by a branching ratio between the two processes markedly in favor of the charge transfer, which is the essential prerequisite for photovoltaic applications.^{20,25} Both theory and experiment indicate that donor–acceptor distance²⁶ and orientation play a pivotal role in controlling the photoinduced electron transfer and consequently the efficiency of charge separation and the lifetime of the charge separated state. To this end, the groups of R. A. J. Janssen, J. Roncali and co-workers developed a set of complementary dyads, where the β -position of terminal thiophene rings, in a tetrathiophene moiety, was connected to a functionalized fullerene in a single or double fashion.²⁷ The macrocyclic thiophene–fullerene conjugate showed rate constants for energy and charge transfer that were more than one order of magnitude larger than those observed for the flexible system. Schuster and co-workers²⁸ investigated the topological control of the intramolecular electron transfer in a symmetrical *parachute*-shaped porphyrin–fullerene dyad. Molecular modelling suggested that the porphyrin moves over the side of the fullerene sphere, bringing the two in close proximity. The efficient and rapid quenching of the porphyrin luminescence, followed by the formation of either the fullerene excited triplet state or the charge separated state, revealed that the above mentioned conformation facilitates through-space interactions between D and A. Guldi and co-workers²⁹ studied the effect of orientation of a Zn-porphyrin and a fullerene moiety on electron transfer rates: π – π interactions was confirmed to be the crucial parameter that controls rates, efficiency and mechanism of electron transfer from the porphyrin to the fullerene.

In this paper we report the synthesis, electrochemistry and photovoltaic properties of a fullerene–bis(styryl)benzene dyad **1** in which the flexible macrocyclic oxyethylene spacer might allow the two chromophores to arrange in a conformation where the reciprocal orientation and distance are the most favorable for the electron transfer process.

2. Experimental

Syntheses

Materials. All reagents for the synthesis, including dry solvents, were purchased from Aldrich and used without further purification. Bis(phosphonium chloride) **4** was prepared as reported in the literature.³⁰

Instrumentation. Thin layer chromatography (TLC) and column chromatography were performed using a Polygram SilG/UV254 (TLC plates) and silica gel MN 60 (70–230 mesh) by Macherey-Nagel. ¹H (250.1 MHz) and ¹³C (62.9 MHz) NMR spectra were recorded on a Bruker AC-F 250 spectrometer. ESI mass spectra were taken on a Thermo Finnigan AQA LC/MS: –4 kV spray voltage; –10 V capillary voltage; 180 °C capillary temperature; nitrogen as nebulizing gas. The samples were dissolved in methanol containing 1% trifluoroacetic acid. Exact mass determination was provided by the Washington University Mass Spectrometry Resource at the Washington University Center for Biomedical and Bioorganic Mass Spectrometry. A matrix of 3-nitrobenzyl alcohol was employed for the measurements. IR spectra were recorded on a Perkin-Elmer FT-IR model 1720X. The UV-Vis spectra were recorded on a Perkin-Elmer Lambda 16 spectrophotometer. The emission spectra were recorded on a Perkin-Elmer LS 55 spectrofluorimeter. HPLC analysis of derivative **1** was performed with a Phenomenex Luna column (250 × 4.6 mm, SiO₂, 5 μ) using toluene–ethyl acetate–isopropanol solvent mixtures: eluent A (toluene–ethyl acetate 8:2), eluent B (toluene–isopropanol 9:1). Linear gradient elution: 100% A for 15 min → 75% A (within 35 min). Flow = 1 ml min^{–1}. In the mentioned HPLC conditions, compound **1** is eluted at 16 min (Fig. S1†).

3-{2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy}-4-methoxybenzaldehyde **2.** A mixture of 3-hydroxy-4-methoxybenzaldehyde (2.0 g, 13.1 mmol) and 2-[2-(2-methoxy)ethoxy]ethyl-*p*-toluenesulfonate (4.0 g, 13.1 mmol) in a suspension of dry K₂CO₃ (5.44 g, 39.4 mmol) in acetone was stirred for 12 h at reflux temperature, and monitored by TLC (eluent: ethyl acetate–hexane 9:1, *R*_f (**2**) = 0.15). The mixture was then concentrated under reduced pressure and the crude product, treated with 30 ml of CHCl₃, washed with 1 M NaOH. The product was purified by flash column chromatography (SiO₂, ethyl acetate–petroleum ether 9:1 then ethyl acetate–ethanol 9:1) affording 3.32 g (89%) of a yellowish oil. IR (nujol) ν 2932, 2876, 1685, 1596, 1587, 1514, 1438, 1268, 1137, 1072, 1022 cm^{–1}. ¹H-NMR (CDCl₃, 250 MHz) δ (ppm): 9.60 (s, 1H), 7.26–7.22 (m, 2H), 6.78–6.74 (d, 1H), 4.01 (t, 2H), 3.70 (s, 3H), 3.69 (t, 2H), 3.51–3.45 (m, 6H), 3.38 (t, 2H), 3.17 (s, 1H). ¹³C-NMR (CDCl₃, 62.9 MHz) δ (ppm) 190.43, 154.37, 148.24, 129.38, 126.35, 110.52, 110.33, 72.10, 70.25, 69.77, 68.86, 67.86, 61.03, 55.52. ESI-MS (C₁₄H₂₀O₆) *m/z* 307 [M + Na]⁺.

3-(2-{2-[2-(*tert*-Butyldimethylsilyloxy)ethoxy]ethoxy}ethoxy)-4-methoxybenzaldehyde **3.** To a solution of benzaldehyde-alcohol **2** (3.0 g, 10.5 mmol) and imidazole (0.78 g, 11.5 mmol) in dry CH₂Cl₂ (40 ml), a solution of *tert*-butyldimethylsilylchloride (1.74 g, 11.5 mmol) in dry CH₂Cl₂ (10 ml) was added dropwise over a period of 15 min, and the reaction was monitored by TLC (eluent: hexane–ethyl acetate 1:9, *R*_f (**3**) = 0.95). When the addition was complete, the mixture was stirred for 5 hours at room temperature, then the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (SiO₂, ethyl acetate–petroleum ether 7:3) yielding 3.64 g (82%) of **3** as a colorless oil. IR (nujol) ν 2953, 2929, 2858, 1689, 1597, 1587, 1513,

1436, 1269, 1253, 1164, 1139, 1108, 837, 779 cm^{-1} . $^1\text{H-NMR}$ (250 MHz, CDCl_3) δ (ppm) 9.78 (s, 1H), 7.43–7.39 (m, 2H), 6.94–6.91 (d, 1H), 4.19 (t, 2H), 3.89 (s, 3H), 3.87 (t, 2H), 3.71–3.64 (m, 6H), 3.51 (t, 2H), 0.84 (s, 9H), 0.01 (s, 6H). $^{13}\text{C-NMR}$ (62.9 MHz, CDCl_3) δ (ppm) 190.69, 154.80, 148.78, 129.85, 126.66, 110.97, 110.61, 72.56, 70.76, 70.62, 69.31, 68.33, 62.58, 55.95, 25.78, 18.22, –5.40. ESI-MS ($\text{C}_{20}\text{H}_{34}\text{SiO}_6$) m/z 421 $[\text{M} + \text{Na}]^+$.

Bis(styryl)benzene 6. To a solution of 2.0 g (5.02 mmol) of benzaldehyde **3** and 1.73 g (2.28 mmol) of 2,5-methoxy-1,4-methyltriphenylphosphonium chloride **4** in 15 ml of absolute ethanol, 9.50 ml of lithium *tert*-butoxide solution (1.0 M in ethanol) were added through a syringe under a nitrogen atmosphere. The solution was stirred for 12 hours at room temperature (TLC, eluent: hexane–ethyl acetate 7:3; broad spot with a retention factor of about 0.5 for the presence of a mixture of isomers) then the solvent was removed *in vacuo*. The residue was passed through a pad of SiO_2 (eluent: petroleum ether–ethyl acetate 8:2) and concentrated under reduced pressure. Conversion of the mixture to the most stable *trans-trans* isomer **5** was accomplished with iodine in refluxing toluene over 4 hours. Derivative **5** was used for the deprotection step without further purification. (An analytical sample of compound **5** can be obtained through flash chromatography purification of crude **5** over SiO_2 ; eluent: petroleum ether–ethyl acetate 8:2). IR (nujol) ν 2928, 2856, 1512, 1265, 1138, 1106, 1042 cm^{-1} . $^1\text{H-NMR}$ (250 MHz, CDCl_3) δ (ppm) 7.35–7.28 (d, 2H, $^3J_{\text{HH}} = 16.5$ Hz), 7.16–7.07 (m, 4H), 7.11 (s, 2H), 7.07–7.01 (d, 2H, $^3J_{\text{HH}} = 16.5$ Hz), 6.87–6.83 (d, 2H), 4.26 (t, 4H), 3.95 (t, 4H), 3.92 (s, 6H), 3.87 (s, 6H), 3.81–3.70 (m, 12H), 3.59–3.55 (m, 4H), 0.88 (s, 9H), 0.06 (s, 6H). $^{13}\text{C-NMR}$ (62.9 MHz, CDCl_3) δ (ppm) 151.25, 149.34, 148.29, 132.94, 130.96, 129.60, 126.32, 121.28, 120.44, 111.70, 111.34, 108.81, 72.60, 70.81, 69.59, 68.42, 66.59, 62.63, 56.21, 55.88, 25.84, 18.27, 5.35. ESI-MS ($\text{C}_{50}\text{H}_{78}\text{Si}_2\text{O}_{12}$) m/z 949 $[\text{M} + \text{Na}]^+$. To crude derivative **5**, dissolved in 10 ml of dry THF, tetrabutylammonium fluoride (0.66 ml, 2.2 mmol) was added under nitrogen. The resulting mixture was stirred for 5 hours at room temperature (TLC, eluent: ethyl acetate–ethanol 9:1, R_f (**6**) = 0.4), then the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (eluent: ethyl acetate) affording 500 mg of unprotected bis(styryl)benzene **6** (33% overall yield calculated from **3**) as yellow crystals. IR (KBr) ν 3417, 3366, 2924, 2856, 1517, 1499, 1465, 1444, 1410, 1268, 1235, 1211, 1138, 1042, 1020 cm^{-1} . $^1\text{H-NMR}$ (250 MHz, CDCl_3) δ (ppm): 7.34–7.28 (d, 2H, $^3J_{\text{HH}} = 16.5$ Hz), 7.16–7.07 (m, 4H), 7.10 (s, 2H), 7.07–7.00 (d, 2H, $^3J_{\text{HH}} = 16.5$ Hz), 6.87–6.84 (d, 2H), 4.26 (t, 4H), 3.93 (t, 4H), 3.92 (s, 6H), 3.88 (s, 6H), 3.79–3.71 (m, 12H), 3.64–3.60 (t, 4H). $^{13}\text{C-NMR}$ (62.9 MHz, CDCl_3) δ (ppm): 151.32, 149.25, 148.23, 131.05, 128.55, 126.41, 121.38, 120.55, 111.70, 111.20, 108.93, 72.63, 70.83, 70.31, 69.68, 68.36, 61.78, 56.32, 55.93. ESI-MS ($\text{C}_{38}\text{H}_{50}\text{O}_{12}$) m/z : 721 $[\text{M} + \text{Na}]^+$.

Macrocyclic bis(styryl)benzene 7. To a stirred suspension of NaHCO_3 (26 mg, 0.31 mmol) in CH_2Cl_2 (20 ml), a solution of derivative **6** (100 mg, 0.14 mmol) in 10 ml of CH_2Cl_2 and a solution of malonyl dichloride (30 μL , 0.31 mmol) in 10 ml of

dry CH_2Cl_2 were added dropwise over a period of 1 h under a nitrogen atmosphere. When the addition was complete, the mixture was stirred at room temperature for 4 h, then the solvent was removed *in vacuo* (TLC, eluent: ethyl acetate–hexane 9:1, R_f (**6**) = 0.5). The residue was purified by flash column chromatography (eluent: ethyl acetate–petroleum ether 8:2) to give 39 mg (36%) of product **7** as a yellow solid. IR (KBr) ν 3419, 3053, 3003, 2925, 1516, 1266, 1229, 1211, 1138, 1105, 1062, 1043 cm^{-1} . UV-Vis (CH_2Cl_2) λ 398, 342 nm. $^1\text{H-NMR}$ (250 MHz, CDCl_3) δ (ppm): 7.43–7.42 (m, 2H), 7.35–7.29 (d, 2H, $^3J_{\text{HH}} = 16.5$ Hz), 7.10 (s, 2H), 7.08–7.02 (d, 2H, $^3J_{\text{HH}} = 16.5$ Hz), 7.08–7.07 (m, 2H), 6.87–6.83 (m, 2H), 4.39 (t, 4H), 4.21 (t, 4H), 3.92 (s, 6H), 3.88 (s, 6H), 3.88–3.84 (m, 12H), 3.67–3.64 (m, 4H), 3.30 (s, 2H). $^{13}\text{C-NMR}$ (62.9 MHz, CDCl_3) δ (ppm): 166.44, 151.29, 149.54, 148.21, 131.07, 128.63, 126.38, 121.56, 120.71, 113.33, 111.51, 109.00, 68.92, 68.75, 64.31, 56.27, 55.91. ESI-MS ($\text{C}_{41}\text{H}_{50}\text{O}_{14}$) m/z 766 $[\text{M}]^+$.

Macrocyclic methanofullerene 1. To a solution of bis(styryl)benzene **7** (39 mg, 0.51 mmol), C_{60} (44 mg, 0.61 mmol) and iodine (14 mg, 0.61 mmol) in toluene (30 ml), a solution of DBU (11 μL , 0.72 mmol) in 5 ml of toluene was added dropwise over a period of 15 minutes. When the addition was complete, the mixture was stirred at room temperature for 4 hours, then the solvent was removed under reduced pressure (TLC, eluent: toluene–ethanol 95:5, R_f (**1**) = 0.55). The product was purified by flash column chromatography (eluent: toluene then toluene–2-PrOH 9:1), affording 32 mg (42%) of pure **1** as a brownish solid compound. IR (KBr) ν 3453, 3441, 2944, 2929, 2868, 1511, 1265, 1231, 1208, 1137, 1114, 1043, 1031, 963, 527 cm^{-1} . UV-Vis (CH_2Cl_2) λ (ϵ) 229 (92879), 256 (111632), 326 (46782 $\text{M}^{-1} \text{cm}^{-1}$) nm. $^1\text{H-NMR}$ (250 MHz, CDCl_3) δ (ppm): 7.39 (m, 2H), 7.33–7.26 (d, 2H, $^3J_{\text{HH}} = 15$ Hz), 7.09 (s, 2H), 7.05–6.99 (d, 2H, $^3J_{\text{HH}} = 15$ Hz), 7.05 (m, 2H), 6.85–6.81 (m, 2H), 4.57 (t, 4H), 4.36 (t, 4H), 3.95 (s, 6H), 3.88 (s, 6H), 3.84–3.79 (m, 12H), 3.64 (m, 4H). $^{13}\text{C-NMR}$ (62.9 MHz, CDCl_3) δ (ppm): 163.5, 151.3, 149.4, 148.2, 145.2, 145.1, 145.0, 144.9, 144.8, 144.6, 144.4, 144.3, 143.7, 142.9, 142.8, 142.7, 142.0, 141.6, 140.7, 138.8, 131.1, 128.8, 126.5, 121.7, 120.6, 113.4, 111.5, 109.0, 71.2, 70.9, 70.6, 70.4, 68.9, 65.9, 56.3, 55.9, 52.4. HR-FAB MS m/z : 1485.2966 (theoretical mass: m/z : 1485.3123; –10.6 ppm).

Cyclic voltammetry experiments

Cyclic voltammetries were performed at room temperature in a three compartment glass electrochemical cell under Ar pressure by using a potentiostat/galvanostat AMEL model 5000. The working electrode was a Pt sphere (area 0.13 cm^2), the reference electrode was a saturated calomel electrode (SCE) and the auxiliary electrode was a Pt wire. The support electrolyte was 0.1 M $(\text{C}_4\text{H}_9)_4\text{NClO}_4$ (Fluka, puriss. crystallized from CH_2Cl_2 and vacuum dried) in CH_2Cl_2 (Merck, Uvasol, distilled over P_2O_5 and stored under Ar pressure); before use, the solution was stored for 24 hours over 3 Å molecular sieves (Merck, activated for 4 hours at 380 °C).

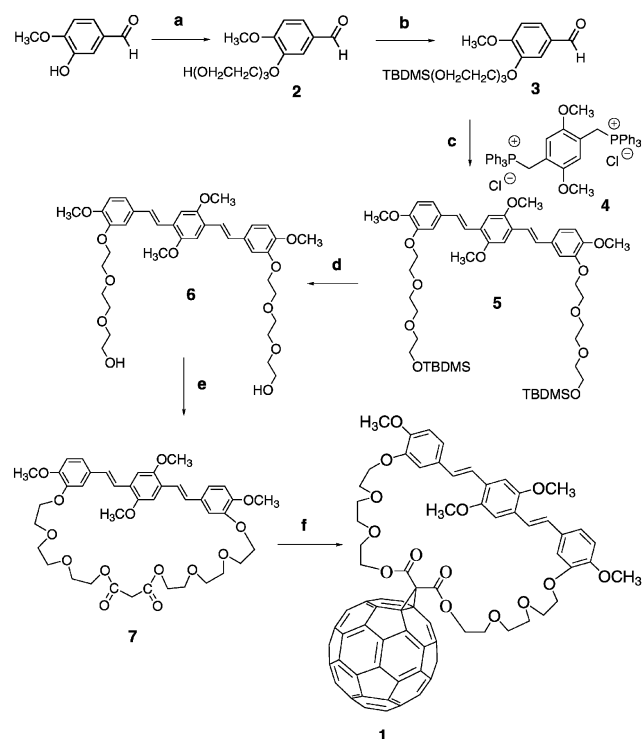
Photovoltaic devices

The photoactive layers were spun at 2000–3000 rpm from chloroform or chlorobenzene solutions (15 g l^{-1}) onto indium

tin oxide (ITO)/glass substrates previously coated with a layer of polystyrene sulfonic acid doped poly(ethylene-dioxythiophene) (PEDOT:PSS, from Bayer AG). The film thicknesses (around 100 nm) were determined using a profilometer Alpha Step 200 (Tencor Instruments). The structure of the photovoltaic devices was completed by subliming an aluminium top electrode *in vacuo*, the active area of the devices was 3.14 mm². Except for the cathode deposition, each step of the device fabrication was performed in ambient conditions. The electrical characterization of the devices was performed with a Keithley 2400 source measure unit, under a dynamic vacuum of 2×10^{-4} mbar, in a home made chamber. Junctions were illuminated through the ITO side with a 300 W Xe arc lamp. The intensity of the incident light (86 mW cm⁻²) was measured with an Oriel thermopile. No correction was made for light reflection. The optical bench was equipped with a water filter to cut off IR radiation.

3. Results and discussion

The synthesis of the macrocyclic methanofullerene **1** is illustrated in Scheme 1. It began with compound **2**, which was prepared in 89% yield through a Williamson reaction between 3-hydroxy-4-methoxybenzaldehyde and 2-[2-(2-methoxy)ethoxy]ethyl-*p*-toluenesulfonate in the presence of K₂CO₃. Treatment of **2** with *tert*-butyldimethylsilylchloride (TBDMSCl) and imidazole in CH₂Cl₂ afforded the protected alcohol-aldehyde **3** in 82% yield. This was used for the Wittig



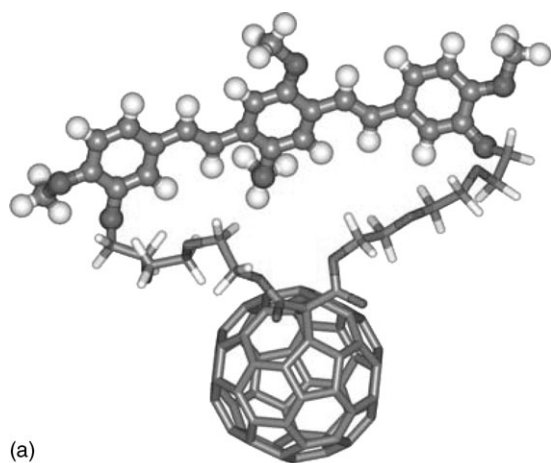
Scheme 1 Synthesis of fullerene-bis(styryl)benzene dyad **1**: (a) 2-[2-(2-methoxy)ethoxy]ethyl-*p*-toluenesulfonate, K₂CO₃, acetone, reflux, 12 h, 89%; (b) TBDMSCl, imidazole, CH₂Cl₂, 25 °C, 5 h, 82%; (c) 2,5-methoxy-1,4-methyltriphenylphosphonium chloride **4**, EtOH, *t*-BuO-Li, 25 °C, 5 h; (d) Bu₄NF, THF, 25 °C, 4 h, 33% calculated from **3**; (e) malonyl dichloride, NaHCO₃, CH₂Cl₂, 1 h, 36%; (f) C₆₀, 1,8-diazabicyclo[5.4.0]undec-7-ene, I₂, toluene, 25 °C, 3 h, 42%.

coupling reaction with bis(phosphonium chloride) **4**, followed by isomerization of the crude mixture with iodine in refluxing toluene to afford the *trans-trans* bis(styryl)benzene **5**. The configuration of the double bonds in **5** was established *via* NMR spectroscopy, through the measurement of the ³J_{HH} of the olefin protons which was found to be around 16 Hz, in line with literature data for olefin *trans* protons.³¹ Removal of the TBDMS groups from **5** with tetrabutylammonium fluoride gave deprotected bis(alcohol) **6** in 33% overall yield calculated from **3**.

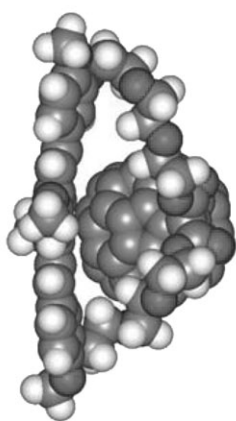
Compound **6**, in the presence of malonyl dichloride and sodium bicarbonate in CH₂Cl₂, afforded the product of macrocyclization **7** in 36% isolated yield. Functionalization of C₆₀ with the cyclic bis(styryl)benzene-malonate derivative **7** was based on the nucleophilic Bingel cyclopropanation of the fullerenes.³² The reaction of C₆₀ and **7** in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene and I₂ in toluene at room temperature afforded methanofullerene **1** in 42% isolated yield. The presence of the oxyethylene groups confers to compound **1** a good solubility in some organic solvents, such as CHCl₃, tetrahydrofuran, chlorobenzene or toluene. HPLC analysis was employed to assess the purity of derivative **1** (Fig. S1†) whereas NMR spectroscopy and exact mass determination were used to validate its proposed molecular structure (Fig. S2–S3†). The symmetry of compound **1** is indicated by its NMR spectra. The ¹³C spectrum shows 28 signals (12 signals are attributed to the bis(styryl)benzene moiety and 16 to the fullerene sphere) between δ 165 and 105, as well as 9 signals in the aliphatic region. The two sp³ fullerene carbons resonate at δ 71.2, together with the adjacent spiro carbon at δ 52.4. The structure of **1** is confirmed by HR-FAB mass spectrometry with the molecular ion peak at *m/z* = 1485.2966 (theoretical mass: *m/z* = 1485.3123).

The geometry of the fullerene dyad **1** was optimized using an ONIOM multilayer model, as implemented in the GAUSSIAN 03 program package.³³ The structure of **1** was partitioned into two layers. The bis(styryl)benzene moiety was treated at the DFT level of theory, using the Becke three-parameter Lee–Yang–Parr (B3LYP) exchange correlation potential, through which electron correlation effects are included, with a 3-21G* basis set. The methanofullerene with the oxyethylene chains was considered as the outer layer and described by a computationally less demanding, semi-empirical method (AM1). The mentioned calculations showed that the bis(styryl)benzene moiety in **1** retains its planar and conjugated molecular structure, with no major distortions induced by the macrocyclic structure (Fig. 1). As a consequence, no meaningful perturbation of its electronic properties is expected because of the covalent linkage to the acceptor moiety.

It is interesting to note that molecular modelling studies on dyad **1** revealed that, in its lowest-energy conformation, the bis(styryl)benzene moiety does not stay above but lies on a side of the fullerene sphere, in a minimum energy conformation that brings the two chromophores in close proximity [Fig. 1(b)]. However, both ¹H and ¹³C the NMR spectra of **1** are consistent with a C_{2v} symmetrical structure, thus suggesting that the bis(styryl)benzene moves back and forth at room temperature from one side of the fullerene to the other. This



(a)



(b)

Fig. 1 (a) ONIOM(B3LYP/3-21G*:AM1) optimized geometry of fullerene dyad **1** (high level represented in ball and stick style; low level AM1 in tube style). (b) Top view (space-filling) of the fullerene dyad **1** represented in (a).

phenomenon has been already documented for a porphyrin-methanofullerene dyad.²⁸

The absorption spectrum of dyad **1** in dichloromethane (Fig. 2) is the superposition of the absorption features of the

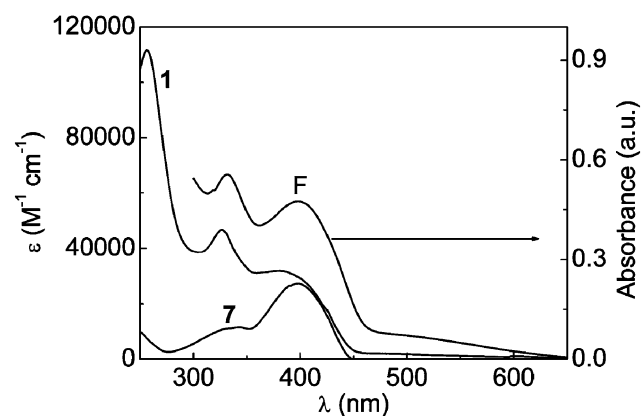


Fig. 2 Absorption spectra of the macrocyclic dyad **1** and of the bis(styryl)benzene precursor **7** in CH_2Cl_2 . The spectrum of a 100 nm thick film of **1**, onto glass/ITO substrate, is also shown (F) for comparison.

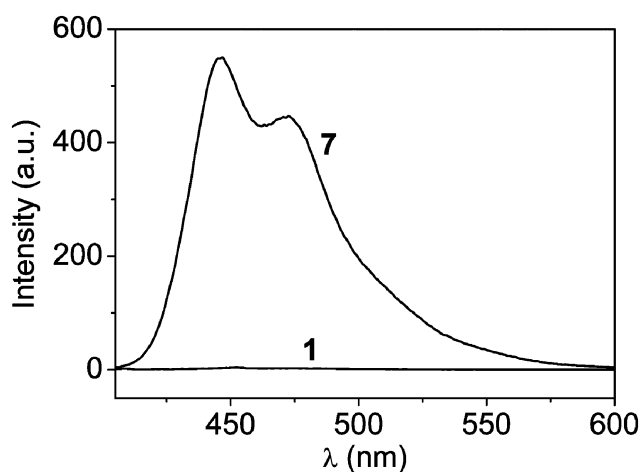


Fig. 3 Fluorescence spectra of the macrocyclic dyad **1** and of the bis(styryl)benzene precursor **7** in CH_2Cl_2 at 25 °C.

bis(styryl)benzene and fullerene chromophores, indicating a negligible interaction between the two components in the ground state. This is in agreement with the voltammetric results (*vide infra*).

Emission measurements with dyad **1** and model **7** were carried out in CH_2Cl_2 at 25 °C. Excitation of **7** ($\lambda_{\text{exc}} = 400$ nm) produces a strong emission band with a maximum at around 445 nm (Fig. 3). A solution of dyad **1**, with equal absorbance at $\lambda_{\text{exc}} = 400$ nm, shows a remarkable quenching of the previously mentioned 445 nm emission.

The voltammogram of **1** (Fig. 4) shows three reduction waves at negative potentials (marked with 1 to 3 in Fig. 4), that are due to the methanofullerene moiety, and two oxidation waves (4 and 5) in the region of positive potentials.

The voltammogram of **7** does not show reduction waves up to the electrolyte breakdown at negative potentials but it shows two oxidation waves, close to those observed for dyad **1**, in the region of positive potentials. The voltammetric waves

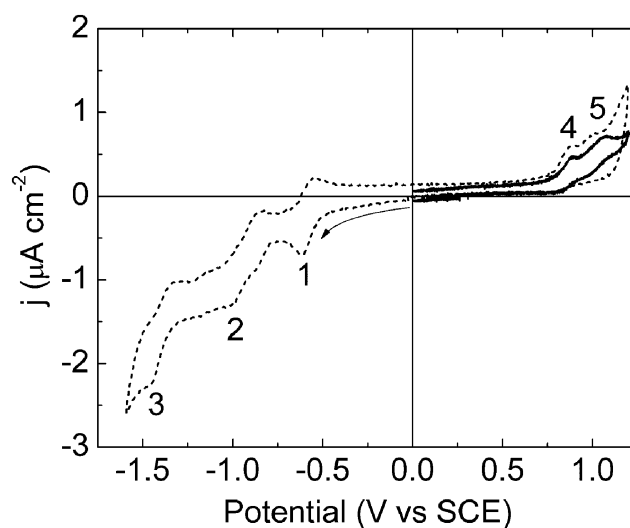


Fig. 4 Cyclic voltammograms at 20 mV s^{-1} of **1** (dashed line) and **7** (full line) 0.5 nM in $\text{CH}_2\text{Cl}_2-(\text{C}_4\text{H}_9)_4 \text{N ClO}_4$ 0.1 M.

Table 1 Redox potentials (V vs. SCE) from cyclic voltammetries at 20 mV s⁻¹ of 0.5 mM solutions in CH₂Cl₂-(C₄H₉)₄NClO₄ 0.1 M

Compound	$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(3)$	$E_{1/2}(4)$	$E_{1/2}(5)$
1	-0.59	-0.93	-1.40	+0.83	+1.03 ^a
7	—	—	—	+0.84	+1.02

^a Maximum potential of the oxidation wave 5 [$E_o(5)$].

1 and **4** appear reversible, in fact the differences between the maximum potential of the oxidation waves [$E_o(i)$, where i is the marker of the wave, in this case $i = 1$ and $i = 4$] and the minimum potential of the related reduction waves [$E_r(i)$, in this case $E_r(1)$ and $E_r(4)$] are very close to 59 mV. Waves 2 and 3 appear quasi-reversible, likely because of follow-up reactions associated to electrochemically-induced opening of the cyclopropane ring, as typically observed in malonate-fullerenes.³⁴

Table 1 summarizes the redox potentials $E_{1/2}(i) = [E_o(i) - E_r(i)]/2$ that are in reasonable agreement with the values recorded at 0.1 V s⁻¹ for pristine fullerene in the same electrolyte,³⁵ if the small influence of the derivatization of **1** on the redox potentials of the methanofullerene moiety is taken into account.³⁶ In fact, the functionalization of fullerene, leading to methanofullerene C₆₁H₂, introduces a potential shift estimated at 120 mV, but larger potentials shift are expected if stronger electron donors are attached.³⁷ Furthermore, within the experimental uncertainty, $E_{1/2}(4)$ and $E_{1/2}(5)$ of **1** are equal to those of **7**, confirming that electronic interactions between methanofullerene and bis(styryl)benzene moieties are negligible, as already reported for oligophenylenevinylene–fulleropyrrolidine dyads.^{19b,19f}

Dyad **1** has excellent film forming properties, an imperative requisite for high performance photovoltaic devices, when deposited from chlorinated solutions. The surface morphology of films of dyad **1**, spun onto ITO/PEDOT:PSS substrates from chloroform or chlorobenzene solutions, was investigated by means of scanning force microscopy and the images (not shown here) revealed a fairly smooth surface, as already observed for films of other fullerene dyads.²³

Photovoltaic cells were realized, using the ITO/PEDOT:PSS/**1**/Al configuration, to test the photoresponse of the dyad. The devices were prepared at ambient conditions, apart from the cathode deposition, and tested in dynamic vacuum (2×10^{-4} mbar). Junctions with good rectification properties were obtained. A typical current–voltage curve in the dark is reported in Fig. 5(a). Under white-light irradiation of intensity 86 mW cm⁻² they gave current–voltage curves as shown in Fig. 5(b), with a short-circuit current (j_{sc}) of 9.3×10^{-5} A cm⁻², an open-circuit voltage (V_{oc}) of 0.68 V and a fill factor (FF) of 0.30. The values for V_{oc} and FF are respectively the highest and among the highest reported for OPV–fullerene dyads. The overall white-light conversion efficiency (η) calculated for the devices was 0.022%. This is, to our knowledge, the highest value reported in the literature, for cells based on dyads which contain a fullerene tethered to an oligo(phenylene)vinylene, obtained under high level irradiation conditions (not lower than 80 mW cm⁻²). Solar cells whose active layer was spun from chlorobenzene exhibited the same performance of those spun from chloroform.

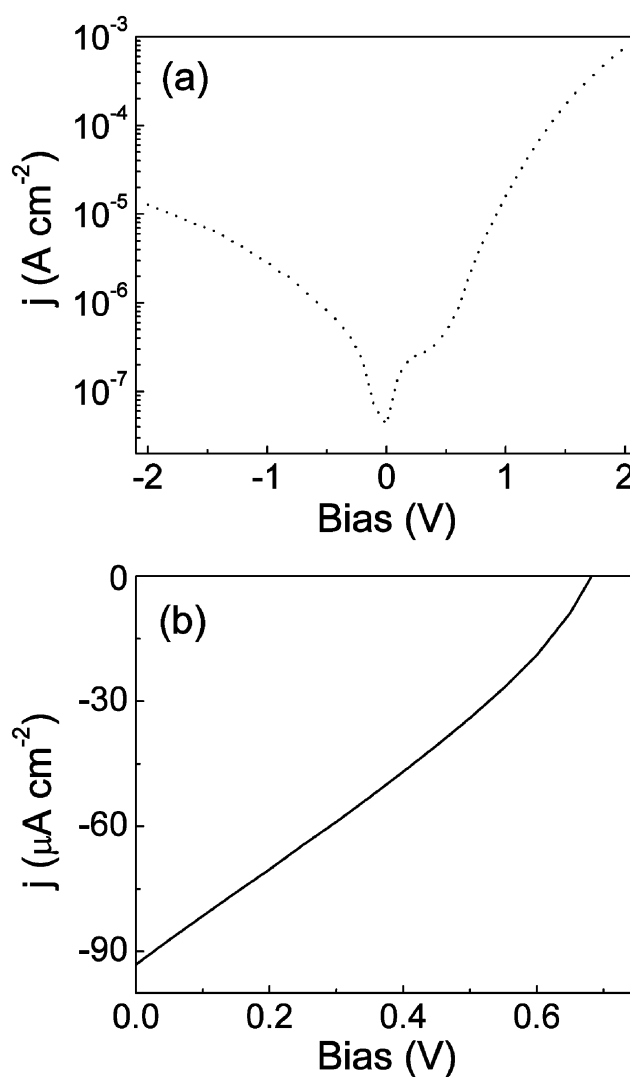


Fig. 5 Current–voltage curves of an ITO/PEDOT:PSS/**1**/Al cell in the dark (a) and under 86 mW cm⁻² white light irradiation (b). Photovoltaic parameters: $j_{sc} = 9.3 \times 10^{-5}$ A cm⁻²; $V_{oc} = 0.68$ V; $FF = 0.30$; $\eta = 0.022\%$. The active layer was spun from CHCl₃. Room temperature.

Conclusion

In summary, we have found that a macrocyclic bis(styryl)benzene-linked fullerene works as an active component in solar cells. The photovoltaic power conversion efficiency, far from being attractive to the market, represents nevertheless the highest value reported at solar irradiation levels for cells based on dyads in which a fullerene is tethered to a phenylenevinylene structure. In particular, the limited conformational freedom between the fullerene and bis(styryl)benzene units in **1**, if compared to other reported oligo(phenylene)vinylene–fullerene dyads, could play a favourable role in the transport properties of the solar cell. It is worth underlining that the intrinsic fullerene/bis(styryl)benzene moiety weight ratio of 1.8 in dyad **1** is significantly lower than the optimized fullerene/polymer weight ratio of 4, presently used in the most efficient MDMO-PPV/fullerene derivative solar cells.⁶ This might be a

factor limiting the intrinsic efficiency of devices based on dyad **1** compared to that of the corresponding fullerene-PPVs blends, although a competition between energy transfer and electron transfer cannot be ruled out. Furthermore, because of the limited length of the bis(styryl)benzene structure, the absorption spectrum of **1** (Fig. 2) does not cover the wavelength range of the corresponding polymer, leading to a lower photon collection and hence to a lower overall power conversion efficiency. Further improvement could be expected by the utilization of new fullerene derivatives with a wider absorption spectrum in the visible range.

Acknowledgements

Funding from MIUR (GR/No. PRIN2004035502, RBAU017S8R, RBNE01P4JF) and from ITM-CNR is gratefully acknowledged. We thank M. D'Este for his help in carrying out the fluorescence experiments.

References

- (a) G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science*, 1995, **270**, 1789; (b) N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl, *Science*, 1992, **258**, 1474.
- (a) C. J. Brabec, N. S. Sariciftci and J. C. Hummelen, *Adv. Funct. Mater.*, 2001, **11**, 15–26; (b) H. Hoppe and N. S. Sariciftci, *J. Mater. Res.*, 2004, **19**, 1924; (c) H. Spanggaard and F. C. Krebs, *Sol. Energy Mater. Sol. Cells*, 2004, **83**, 125.
- C. J. Brabec, *Sol. Energy Mater. Sol. Cells*, 2004, **83**, 273.
- (a) *Organic Photovoltaics Concepts and Realization*, ed. C. J. Brabec, V. Dyakonov, J. Parisi, N. S. Sariciftci, Springer, Berlin, 2003, vol. 60; (b) K. M. Coakley and M. D. McGehee, *Chem. Mater.*, 2004, **16**, 4533; (c) S. Sun, Z. Fan, Y. Wang and J. Haliburton, *J. Mater. Sci.*, 2005, **40**, 1429.
- H. Hoppe, T. Glatzel, M. Niggemann, A. Hinsch, M. Ch. Luxn-Steiner and N. S. Sariciftci, *Nano Lett.*, 2005, **5**, 269.
- S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz and J. C. Hummelen, *Appl. Phys. Lett.*, 2001, **78**, 841.
- (a) C.-H. Huang, N. D. McClenaghan, A. Kuhn, J. W. Hofstra and D. M. Bassani, *Org. Lett.*, 2005, **7**, 3409; (b) G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Nat. Mater.*, 2005, **4**, 864; (c) W. Ma, C. Yang, X. Gong, K. Lee and A. J. Heeger, *Adv. Funct. Mater.*, 2005, **15**, 1617.
- (a) *Thin Solid Films*, 2004, **451–452**: special issue on thin solid films and nano-structured materials for photovoltaics (E-MRS 2003 Spring Conference - Symposium D); (b) *Sol. Energy Mater. Sol. Cells*, 2004, **83**: special issue on the development of organic and polymer photovoltaics; (c) *Appl. Phys. A: Mater. Sci. Process.*, 2004, **79**: special issue on organic photovoltaics.
- (a) A. Cravino and N. S. Sariciftci, *J. Mater. Chem.*, 2002, **12**, 1931; (b) A. Cravino and N. S. Sariciftci, *Nat. Mater.*, 2003, **2**, 360.
- X. N. Yang, J. K. J. van Duren, R. A. J. Janssen, M. A. J. Michels and J. Loos, *Macromolecules*, 2004, **37**, 2151.
- (a) T. Benicori, E. Brenna, F. Sannicolò, L. Trimarco, G. Zotti and P. Sozzoni, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 648; (b) J. P. Ferraris, A. Yassar, D. C. Loveday and M. Hmyene, *Opt. Mater. (Amsterdam)*, 1998, **9**, 34; (c) A. Cravino, G. Zerza, M. Maggini, S. Bucella, M. Svensson, M. R. Andersson, H. Neugebauer and N. S. Sariciftci, *Chem. Commun.*, 2000, 2487; (d) B. Jousset, P. Blanchard, E. Levillain, R. de Bettignies and J. Roncali, *Macromolecules*, 2003, **36**, 3020.
- (a) A. Marcos Ramos, M. T. Rispens, J. K. J. van Duren, J. C. Hummelen and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2001, **123**, 6714; (b) F. L. Zhang, M. Svensson, M. R. Andersson, M. Maggini, S. Bucella, E. Menna and O. Inganäs, *Adv. Mater.*, 2001, **13**, 1871.
- J. K. J. van Duren, X. N. Yang, J. Loos, C. W. T. Bulle-Lieuwma, A. B. Sieval, J. C. Hummelen and R. A. J. Janssen, *Adv. Funct. Mater.*, 2004, **14**, 425.
- Fullerenes: Chemistry, Physics, and Technology*, ed. K. M. Kadish and R. S. Ruoff, Wiley, New York, 2000.
- M. Maggini, G. Possamai, E. Menna, G. Scorrano, N. Camaioni, G. Ridolfi, G. Casalbore-Miceli, L. Franco, M. Ruzzi and C. Corvaja, *Chem. Commun.*, 2002, 2028.
- J.-F. Nierengarten, J. F. Eckert, J. F. Nicoud, L. Ouali, V. Krasnikov and G. Hadzioannou, *Chem. Commun.*, 1999, 617.
- (a) J. L. Segura, N. Martín and D. M. Guldi, *Chem. Soc. Rev.*, 2005, **34**, 31; (b) J. Roncali, *Chem. Soc. Rev.*, 2005, **34**, 483; (c) J.-F. Nierengarten, *Sol. Energy Mater. Sol. Cells*, 2004, **83**, 187.
- (a) P. A. van Hal, J. Knol, B. M. W. Langveld-Voss, S. C. J. Meskers, J. C. Hummelen and R. A. J. Janssen, *J. Phys. Chem. A*, 2000, **104**, 5974; (b) J. L. Segura and N. Martín, *Tetrahedron Lett.*, 1999, **40**, 3239; (c) J. J. Aperlóo, C. Martineau, P. A. van Hal, J. Roncali and R. A. J. Janssen, *J. Phys. Chem. A*, 2002, **106**, 21.
- (a) E. Peeters, P. A. van Hal, J. Knol, C. J. Brabec, N. S. Sariciftci, J. C. Hummelen and R. A. J. Janssen, *J. Phys. Chem. B*, 2000, **104**, 10174; (b) J.-F. Eckert, J.-F. Nicoud, J.-F. Nierengarten, S. G. Liu, L. Echegoyen, F. Barigelletti, N. Armaroli, L. Ouali, V. Krasnikov and G. Hadzioannou, *J. Am. Chem. Soc.*, 2000, **122**, 7467; (c) T. Gu, D. Tsamouras, C. Melzer, V. Krasnikov, J.-P. Gisselbrecht, M. Gross, G. Hadzioannou and J.-F. Nierengarten, *ChemPhysChem*, 2002, **3**, 124; (d) N. Armaroli, G. Accorsi, J.-P. Gisselbrecht, M. Gross, V. Krasnikov, D. Tsamouras, G. Hadzioannou, M. J. Gomez-Escalonilla, F. Langa and J.-F. Eckert, *J. Mater. Chem.*, 2002, **12**, 2077; (e) J.-F. Nierengarten, N. Armaroli, G. Accorsi, Y. Rio and J.-F. Eckert, *Chem.-Eur. J.*, 2003, **9**, 34; (f) N. Armaroli, F. Barigelletti, P. Ceroni, J.-F. Eckert, J.-F. Nicoud and J.-F. Nierengarten, *Chem. Commun.*, 2000, 599; (g) J. L. Segura, R. Gomez, N. Martín, C. Luo, A. Swartz and D. M. Guldi, *Chem. Commun.*, 2001, 707; (h) D. M. Guldi, C. Luo, A. Swartz, J. L. Segura, R. Gomez and N. Martín, *J. Am. Chem. Soc.*, 2002, **124**, 10875.
- M. A. Loi, P. Denk, H. Hoppe, H. Neugebauer, C. Winder, D. Meissner, D. Brabec, N. S. Sariciftci, A. Gouloumis, P. Vazquez and T. Torres, *J. Mater. Chem.*, 2003, **13**, 700.
- D. M. Guldi, C. P. Luo, A. Swartz, R. Gomez, J. L. Segura, N. Martín, C. Brabec and N. S. Sariciftci, *J. Org. Chem.*, 2002, **67**, 1141.
- (a) T. Gu and J.-F. Nierengarten, *Tetrahedron Lett.*, 2001, **42**, 3175; (b) A. Atienza, B. Insuasty, C. Seoane, N. Martín, J. Ramey and D. M. Guldi, *J. Mater. Chem.*, 2005, **15**, 124.
- G. Possamai, S. Marcuz, M. Maggini, E. Menna, L. Franco, M. Ruzzi, S. Ceola, C. Corvaja, G. Ridolfi, A. Geri, N. Camaioni, D. M. Guldi, R. Sens and T. Gessner, *Chem.-Eur. J.*, 2005, **11**, 5765.
- I. B. Martini, B. Ma, T. Da Ros, R. Helgeson, F. Wudl and B. J. Schwartz, *Chem. Phys. Lett.*, 2000, **327**, 253.
- J. L. Segura, F. Giacalone, R. Gómez, N. Martín, D. M. Guldi, C. Luo, A. Swartz, I. Riedel, D. Chirvase, J. Parisi, V. Dyakonov, N. S. Sariciftci and F. Padinger, *Mater. Sci. Eng. C*, 2005, **25**, 835.
- (a) D. M. Guldi, F. Giacalone, G. De la Torre, J. L. Segura and N. Martín, *Chem.-Eur. J.*, 2005, **11**, 7199; (b) E. Allard, J. Cousseau, J. Orduna, J. Garin, H. X. Luo, Y. Araki and O. Ito, *Phys. Chem. Chem. Phys.*, 2002, **4**, 5944.
- P. Van Hal, E. H. A. Beckers, S. C. J. Meskers, R. A. J. Janssen, B. Jousset, P. Blanchard and J. Roncali, *Chem.-Eur. J.*, 2002, **8**, 5415, and references cited therein.
- D. J. Schuster, P. Cheng, P. D. Jarowski, D. M. Guldi, C. Luo, L. Echegoyen, S. Pyo, A. R. Holzwarth, S. E. Braslavsky, R. M. Williams and G. Klich, *J. Am. Chem. Soc.*, 2004, **126**, 7257.
- D. M. Guldi, C. Luo, M. Prato, A. Troisi, F. Zerbetto, M. Scheloske, E. Dietel, W. Bauer and A. Hirsch, *J. Am. Chem. Soc.*, 2001, **123**, 9166.
- (a) L. I. Belen'kii, Y. B. Vol'kenshtein and I. B. Karmanova, *Russ. Chem. Rev.*, 1977, **46**, 891; (b) S. Nakatsuji, K. Matsuda, Y. Uesugi, K. Nakashima, S. Akiyama, G. Katzer and W. J. Fabian, *J. Chem. Soc., Perkin Trans. 2*, 1991, 861.
- H. Günther, *NMR Spectroscopy. An Introduction*, J. Wiley and Sons, Chichester, 1980.
- (a) C. Bingle, *Chem. Ber.*, 1993, **126**, 1957; (b) J.-F. Nierengarten, W. Gramlich, F. Cardullo and F. Diederich, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2101.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi,

V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A.

Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision C.02)*, Gaussian, Inc., Wallingford, CT, 2004.

34 M. A. Herranz, F. Diederich and L. Echegoyen, *Eur. J. Org. Chem.*, 2004, 2299.

35 D. Dubois, G. Moninot, W. Kutner, M. T. Jones and K. M. Kadish, *J. Phys. Chem.*, 1992, **96**, 7137.

36 L. Echegoyen and L. E. Echegoyen, *Acc. Chem. Res.*, 1998, **31**, 593.

37 J. Chistumoff, and A. J. Bard, in *Organic Conductive Molecules and Polymers*, ed. H. S. Nalwa, John Wiley & Sons, Chichester, 1997, vol. 1, ch. 7, p. 379.