

Supplementary Material for Energy & Environmental Science  
This journal is (c) The Royal Society of Chemistry 2011

Supplementary Information

To be published in the themed issue on **Carbon Nanostructures for Energy**  
Guest Edited by Professors **Dirk Guldi, Andreas Hirsch and Nazario Martin**

## **Efficient Light harvesting Anionic Heptamethine Cyanine-[60] and [70]Fullerene Hybrids.**

**Carmen Villegas,<sup>a</sup> Evangelos Krokos,<sup>b</sup> Pierre-Antoine Bouit,<sup>c</sup> Juan Luis Delgado,<sup>ac</sup> Dirk M. Guldi,<sup>\*b</sup> Nazario Martín<sup>ac\*</sup>**

<sup>a</sup> *Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria s/n, 28040, Madrid (Spain) Fax: (+34) 91-394-4103, ; Tel: (+34) 91-394-4227;*

*E-mail: [nazmar@quim.ucm.es](mailto:nazmar@quim.ucm.es)*

<sup>b</sup> *Department of Chemistry and Pharmacy & Interdisciplinary Center of Molecular Materials (ICMM) Friedrich-Alexander-University Erlangen-Nuremberg Egerlandstr. 3, 91058 Erlangen (Germany)*

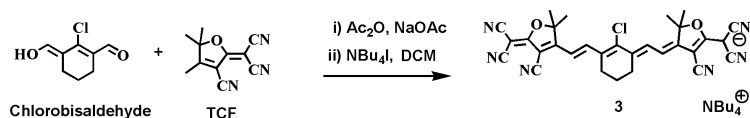
*Fax: (+49) 9131-85-28307*

*E-mail: [dirk.guldi@chemie.uni-erlangen.de](mailto:dirk.guldi@chemie.uni-erlangen.de)*

<sup>c</sup> *IMDEA-Nanociencia, Facultad de Ciencias, Módulo C-IX, 3ª planta, Ciudad Universitaria de Cantoblanco, 28049 Madrid (Spain).*

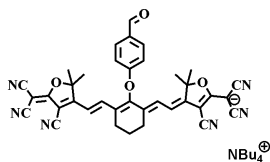
## SYNTHESIS AND CHARACTERIZATION

### Compound 3



Chlorobisaldehyde<sup>1</sup> (217 mg, 1,26 mmol, 1 equiv.) and tricyanofurane<sup>2</sup> (TCF) (502 mg, 2,52 mmol, 2 equiv.) were dissolved in acetic anhydride (20 ml). Sodium acetate was added (360 mg, 2,65 mmol, 2,1 equiv.). The solution was stirred at 150 °C for 30 min. Then the solution was precipitated in a diluted aqueous solution of sodium carbonate. The resulting precipitate was washed with pentane. The crude was filtrated through a plug of silica and washed DCM-MeOH 9:1. The solvents were evaporated to afford the product as a sodium salt. The crude was dissolved in DCM with tetrabutylammonium iodide (1 equiv.). The solution was stirred at room temperature for 15 min. The solution was washed with water (3x30 ml) and dried over MgSO<sub>4</sub>. The solvents were evaporated to afford a dark green solid, **3** (530 mg, 56%). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 300 MHz) δ 8.20 (d, *J*=12 Hz, 2H), 6.08 (d, *J*=12 Hz, 2H), 3.19-3.13 (m, 8H), 2.60-2.56 (m, 4H), 1.78-1.73 (m, 2H), 1.58 (s, 12H), 1.58-1.51 (m, 8H), 1.33-1.24 (m, 8H), 0.93 (t, *J*=7 Hz, 12H). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 75 MHz) δ 176.4, 166.9, 145.8, 139.4, 127.6, 118.0, 115.2, 114.4, 114.3, 107.1, 95.4, 82.6, 57.5, 57.4, 57.3, 54.8, 45.0, 26.1, 25.8, 22.9, 20.4, 19.1, 13.4. FT-IR (KBr): 2210, 1131, 1092 cm<sup>-1</sup>. MS (ESI -): *m/z* calculated for C<sub>30</sub>H<sub>22</sub>ClN<sub>6</sub>O<sub>2</sub><sup>-</sup>: 533,1 [M]<sup>-</sup>: found 533,1.

### Compound 5



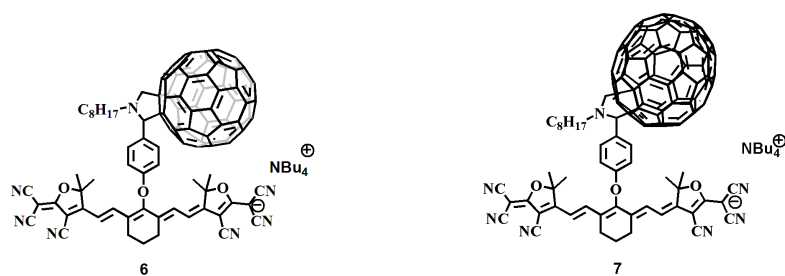
4-(1,3-dioxan-2-yl)phenol (**4**) (87,7 mg, 48 mmol, 1,2 equiv.) was dissolved in dry DMF (20ml) under argon atmosphere, and then NaH 60 % (21 mg, 53 mmol, 1,3 equiv.) was added. After 30 min of stirring at room temperature, **3** (315 mg, 40 mmol, 1 equiv.) dissolved in DMF (20 ml), was added dropwise over this solution. The solution was

<sup>1</sup> G.A. Reynolds, K.H. Drexhage, *J. Org. Chem.*, 1977, **42**, 885.

<sup>2</sup> G. Melikian, F.P. Roussac, C. Alexandre, *Synth. Commun.*, 1995, **25**, 3045.

stirred for 6 h at RT under argon atmosphere, and then poured into ice and hydrochloric acid (1ml). The resulting green solid was filtered off, redissolved in dichloromethane, and washed with water and NaCO<sub>3</sub>. The organic layer was dried with MgSO<sub>4</sub>, and precipitated in pentane, to afford **5** as a green solid (270mg, 75%). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 300 MHz) δ 9.87 (s, 1H), 7.87 (d, *J*=9 Hz, 2H), 7.64 (d, *J*=15 Hz, 2H), 7.14 (d, *J*=9 Hz, 2H), 5.99 (d, *J*=15 Hz, 2H), 3.18-3.13 (m, 8H), 2.63-2.60 (m, 4H), 1.91-1.87 (m, 2H), 1.57-1.54 (m, 8H), 1.39 (s, 12H), 1.39-1.29 (m, 8H), 0.97 (t, *J*=7 Hz, 12H). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 75 MHz) δ 191.4 176.3, 166.5, 163.3, 159.3, 136.4, 132.0, 130.7, 122.7, 115.5, 115.3, 114.4, 114.0, 106.3, 95.2, 82.6, 57.6, 57.5, 57.4, 44.8, 26.1, 23.8, 23.0, 20.6, 19.2, 13.5. UV-Vis (DCM): λ<sub>max</sub>= 896 nm (ε= 300.000 Lxmol<sup>-1</sup>xcm<sup>-1</sup>). FT-IR (KBr): 2209, 1688, 1086, 1045 cm<sup>-1</sup>. MS (ESI -): m/z calculated for C<sub>37</sub>H<sub>27</sub>N<sub>6</sub>O<sub>4</sub><sup>-</sup>: 619,2 [M]<sup>-</sup>: found 619,0.

### Compounds 6 and 7



To a solution of C<sub>60</sub> (for compound **6**) or C<sub>70</sub> (for compound **7**) (0,20 mmol, 3 equiv.) in chlorobenzene, was added *N*-octylglycine (0,07 mmol, 1 equiv.) and compound **5** (0,07 mmol, 1 equiv.). The solution was refluxed for 3 h. Then the solvent was evaporated, and the solid was purified by column chromatography on silica gel (eluent: toluene then DCM-MEOH 9:1). The resulting product was dissolved in the minimum amount of dichloromethane and precipitated in pentane to afford a green solid, **6** or **7** (70 % and 40 % respectively).

Compound **6**: <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 300 MHz) δ 7.76-7.60 (m, 4H), 7.00-6.93 (m, 2H), 5.91 (d, *J*=15 Hz, 2H), 5.12-5.07 (m, 2H), 4.12 (d, *J*=9 Hz, 1H), 3.18-3.13 (m, 8H), 2.59-2.52 (m, 4H), 1.87-1.81 (m, 2H), 1.59-1.53 (m, 8H), 1.37-1.27 (m, 20H), 0.93 (t, *J*=9 Hz, 12H). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 125 MHz) δ 175.9, 166.4, 160.7, 158.9, 156.8, 154.2, 153.6, 147.6, 147.5, 147.3, 147.3, 147.2, 146.9, 146.9, 146.8, 146.8, 146.7, 146.6, 146.5, 146.4, 146.3, 146.1, 146.0, 145.9, 145.7, 145.6, 145.5, 145.5, 145.4, 145.3, 145.2, 145.0, 144.8, 144.6, 144.4, 143.9, 143.8, 143.3, 143.3, 143.3, 142.9,

142.8, 142.7, 142.4, 142.3, 142.1, 142.0, 141.9, 141.8, 141.5, 141.4, 141.2, 140.8, 140.3, 140.3, 140.3, 140.2, 140.2, 139.4, 137.1, 135.9, 135.5, 135.4, 130.2, 122.8, 116.1, 116.1, 116.0, 115.2, 115.1, 115.1, 114.4, 114.4, 114.3, 113.5, 105.9, 94.8, 80.5, 76.6, 68.5, 65.8, 57.5, 52.0, 45.1, 31.3, 28.9, 28.7, 27.5, 27.0, 26.3, 26.1, 23.7, 23.0, 22.1, 20.6, 19.1, 14.0, 13.4. UV-Vis (DCM):  $\lambda_{\max}$  = 896 nm,  $\epsilon$  = 270.000 L $\times$ mol $^{-1}$  $\times$ cm $^{-1}$ . FT-IR (KBr): 2207, 1084, 1043, 523 cm $^{-1}$ . MS (ESI -): m/z calculated for C<sub>106</sub>H<sub>46</sub>N<sub>7</sub>O<sub>3</sub> $^{-}$ : 1465,36999 [M] $^{-}$  found: 1465,35757.

Compound 7: UV-Vis (DCM):  $\lambda_{\max}$  = 896 nm ( $\epsilon$  = 250.000 L $\times$ mol $^{-1}$  $\times$ cm $^{-1}$ ). FT-IR (KBr): 2210, 1085, 1047, 838, 517 cm $^{-1}$ . MS (ESI -): m/z calculated for C<sub>116</sub>H<sub>46</sub>N<sub>7</sub>O<sub>3</sub> 1585,37000 [M] $^{-}$  found: 1585,36895.

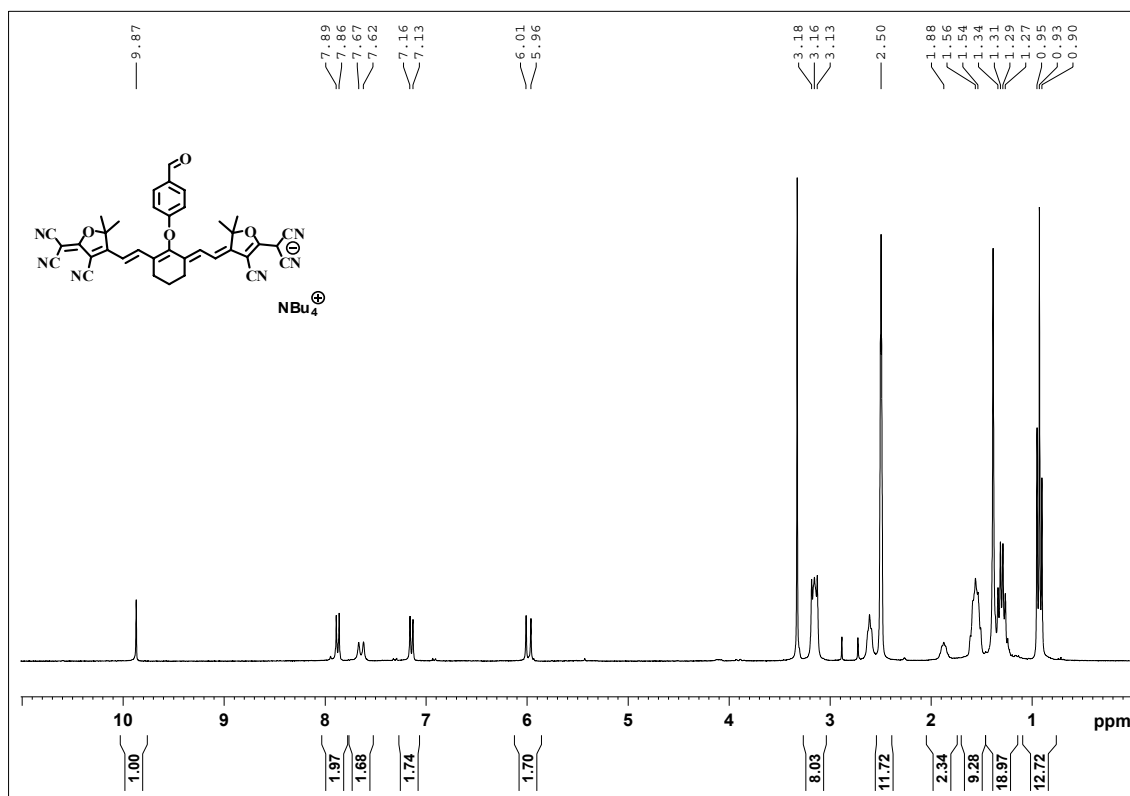


Figure S1: <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 300 MHz) of 5.

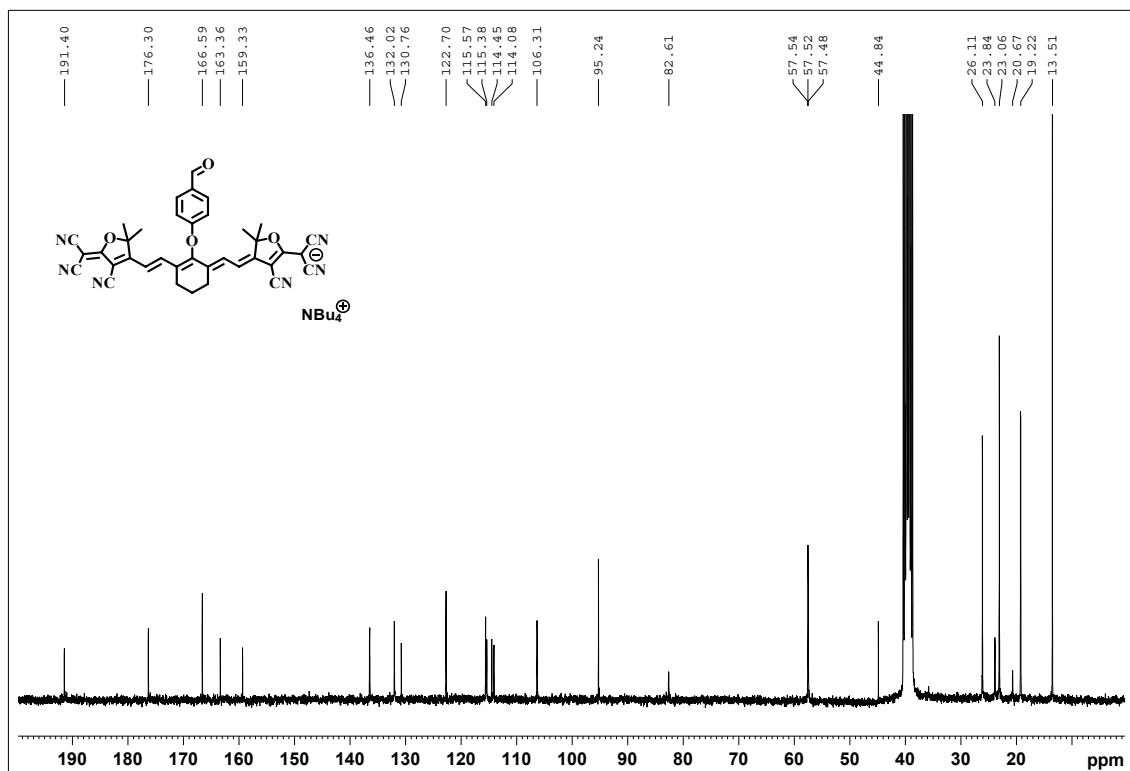


Figure S2: <sup>13</sup>C-NMR(DMSO-*d*<sub>6</sub>, 75 MHz) of **5**.

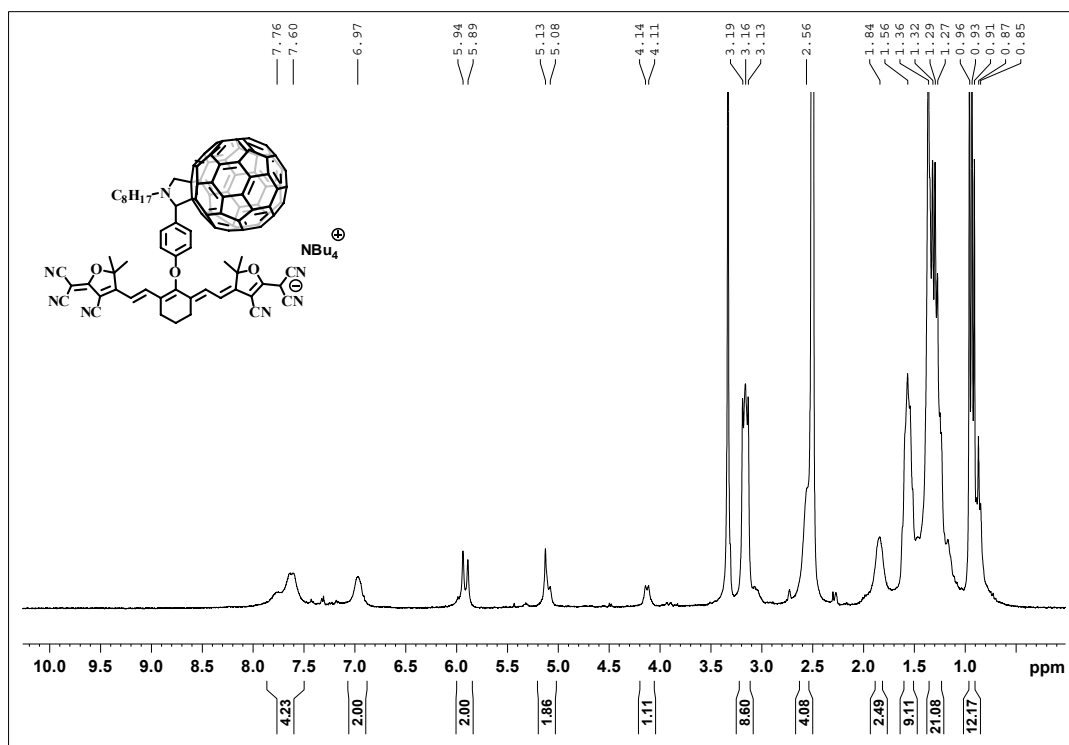


Figure S3: <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 300 MHz) of **6**.

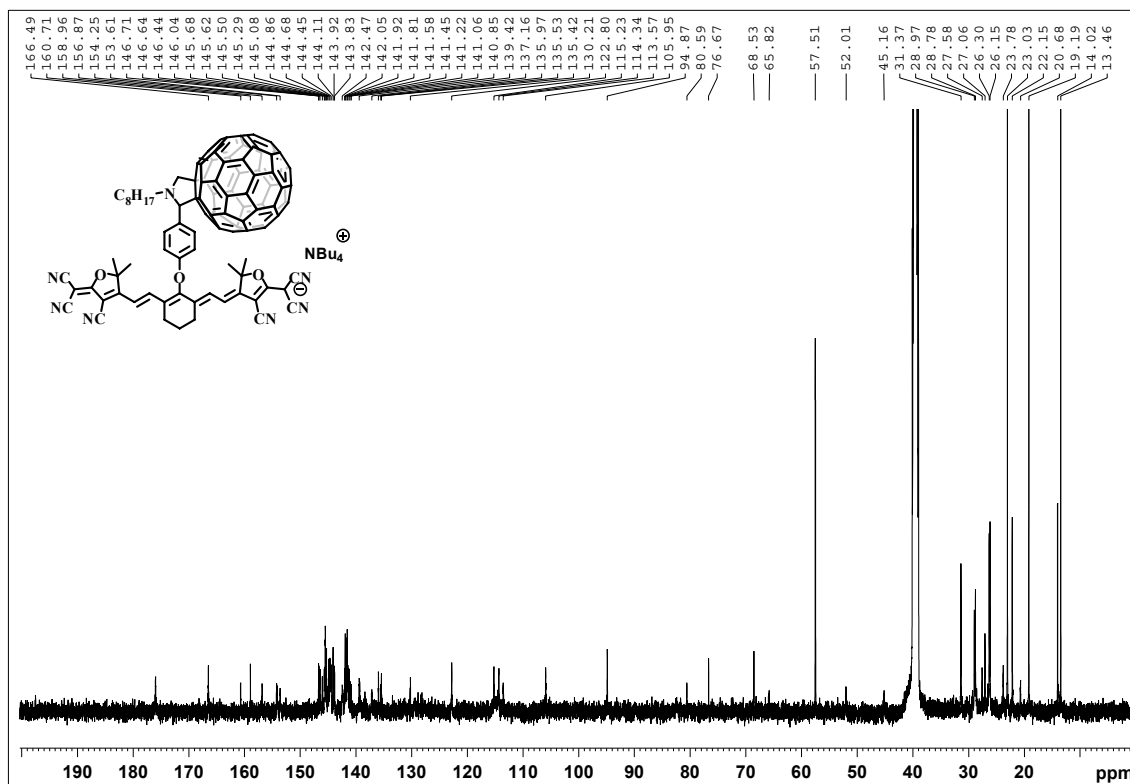


Figure S4:  $^{13}\text{C}$ -NMR (DMSO- $d_6$ , 125 MHz) of **6**.

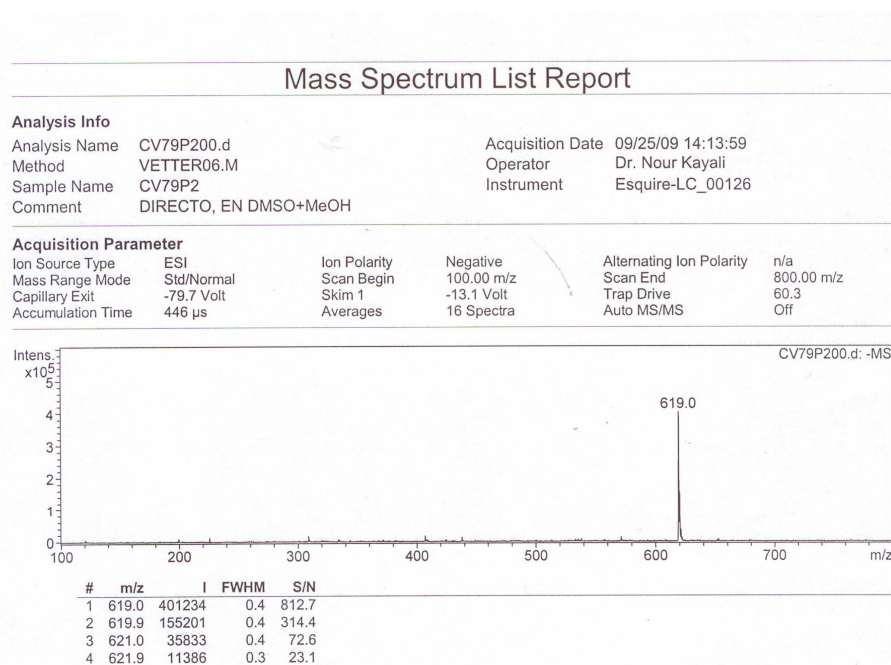


Figure S5: MS of **5**.

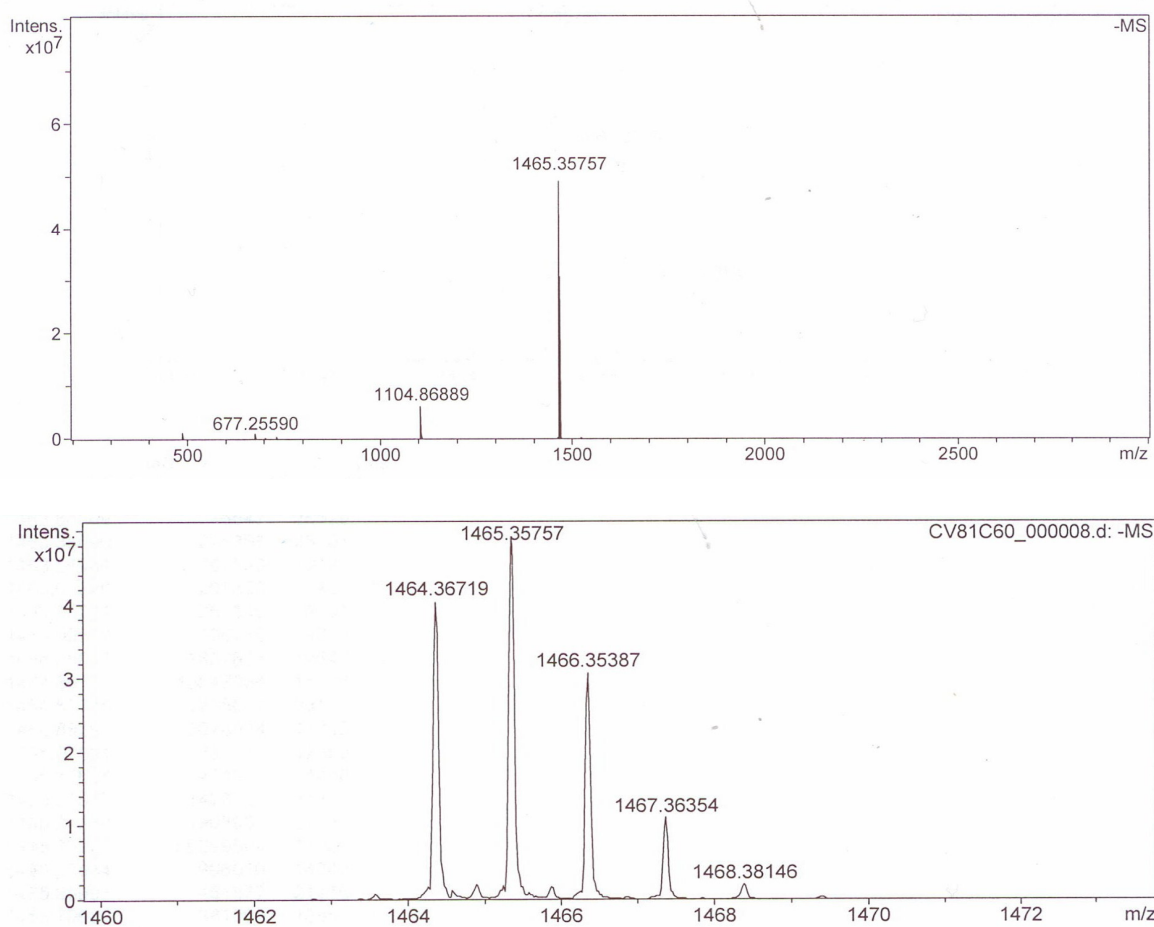


Figure S6: MS of 6.

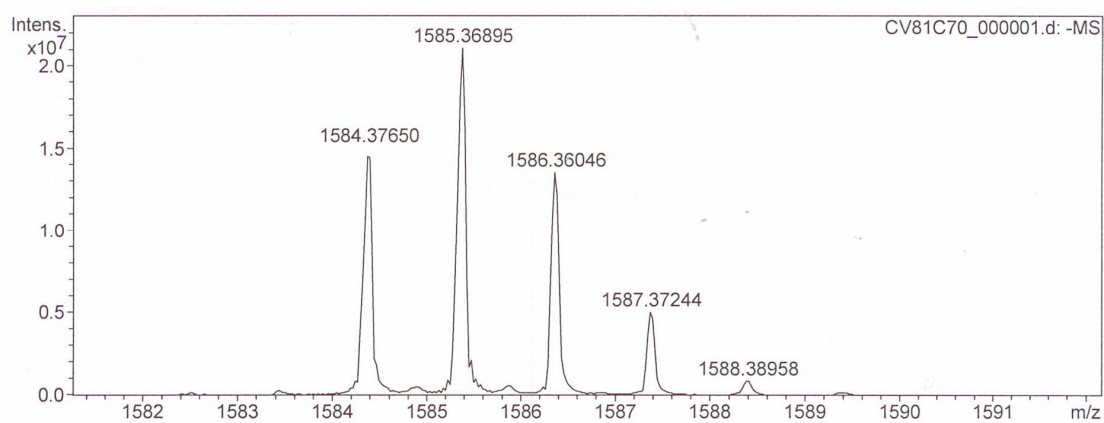
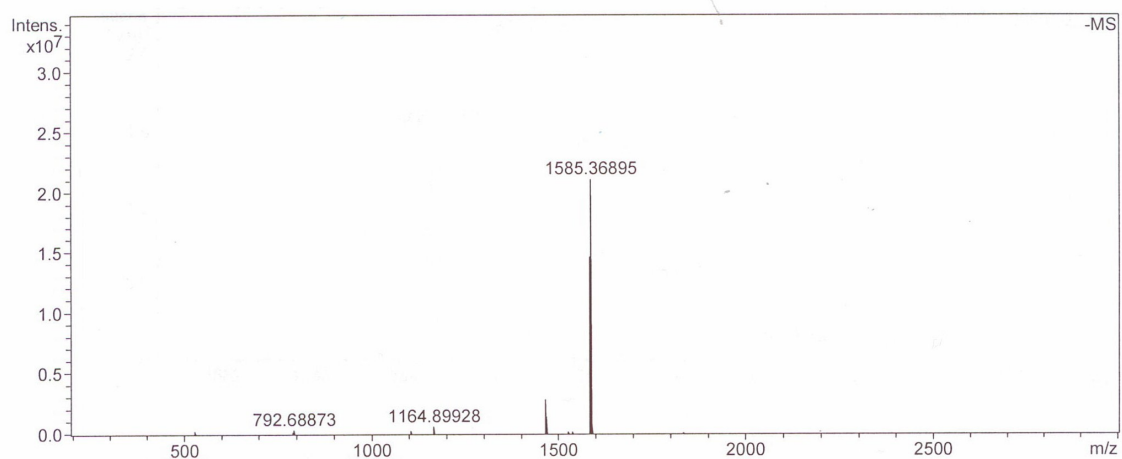


Figure S7: MS of 7.



### ELECTROCHEMISTRY

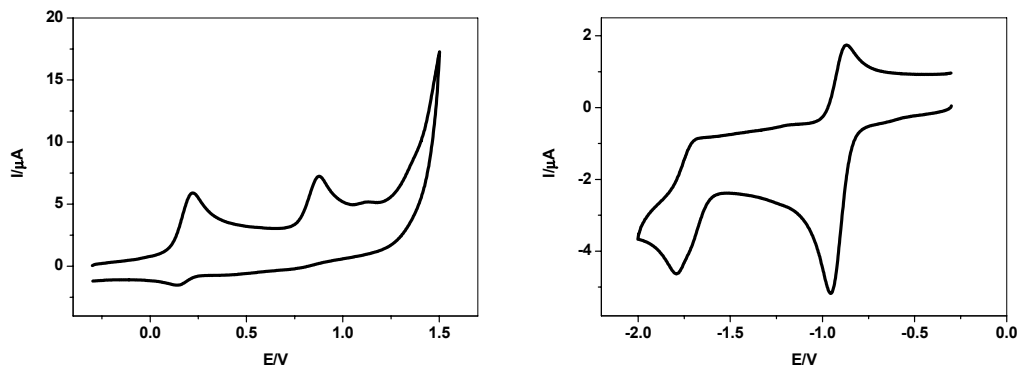


Figure S8: Cyclic voltammograms of **5**. V vs Ag/AgNO<sub>3</sub>; GCE as the working electrode; 0.1 M TBAP; ODCB/MeCN (4:1); scan rate 100 mV/s.

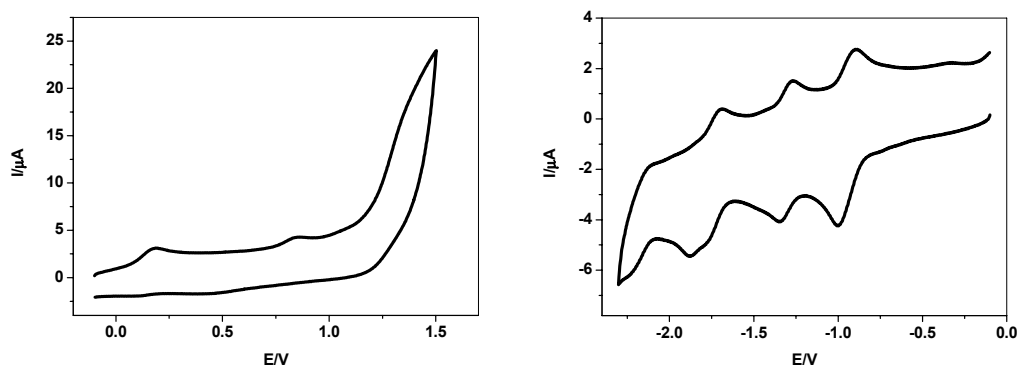


Figure S9. Cyclic voltammograms of **7**. V vs Ag/AgNO<sub>3</sub>; GCE as the working electrode; 0.1 M TBAP; ODCB/MeCN (4:1); scan rate 100 mV/s.

Compound	$E^1_{OX}$	$E^2_{OX}$	$E^1_{RED}$	$E^2_{RED}$	$E^3_{RED}$
<b>1</b>	0,37	0,97	-0,91	-1,31	-1,85
<b>5</b>	0,18	0,87	-0,94	-1,76	
<b>6</b>	0,16	0,88	-0,95	-1,32	-1,88
<b>7</b>	0,16	0,86	-0,94	-1,31	-1,78

Table S1. Redox potentials of **1,5,6** and **7**. V vs Ag/AgNO<sub>3</sub>; GCE as the working electrode; 0.1 M TBAP; ODCB/MeCN (4:1); scan rate 100 mV/s.

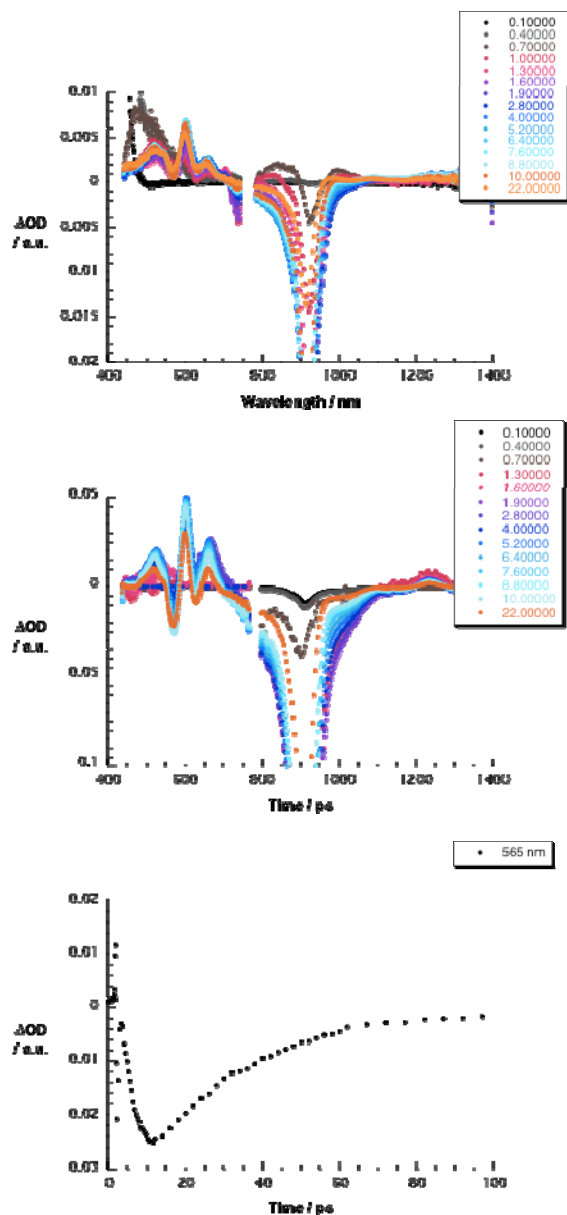


Figure S10: Upper part – differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm) of **7** in benzonitrile with several time delays between 0 and 22 ps at room temperature – see Figure legend for details. Central part – differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (775 nm) of **7** in benzonitrile with several time delays between 0 and 22 ps at room temperature – see Figure legend for details. Lower part – time-absorption profiles of the spectra shown in the central part at 565 nm monitoring the charge separation and charge recombination.

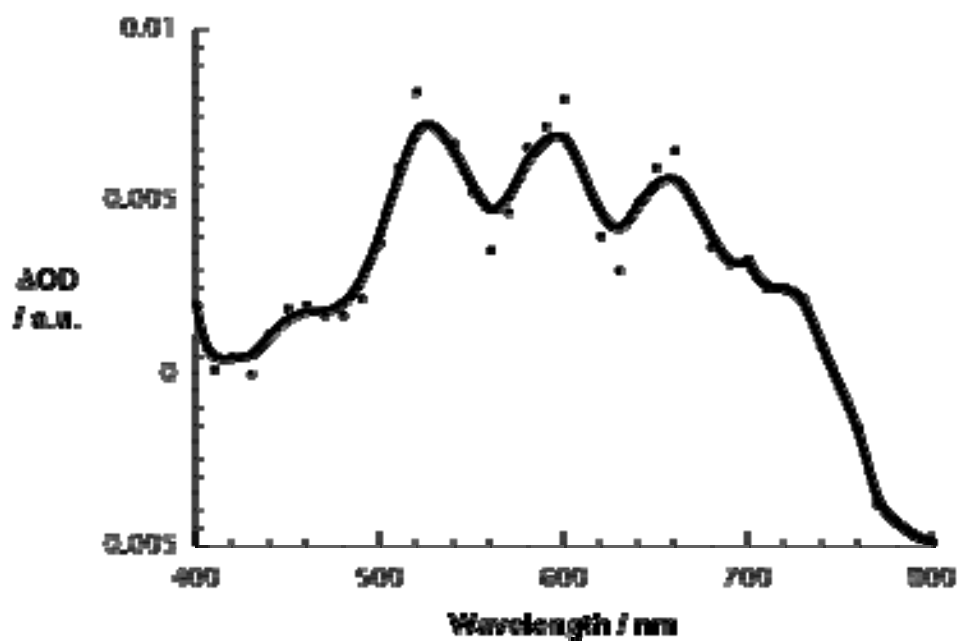


Figure S11. Differential absorption changes following pulse radiolytic oxidation of **5** in oxygenated dichloromethane with  $\cdot\text{OOCH}_2\text{Cl}$  or  $\cdot\text{OOCHCl}_2$ .