

## Supporting Information for

# Core-extended Rylene Dyes via Thiophene Annulation

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## Table of contents

1. Materials and Methods.....	S2
2. Synthesis and characterization of compounds 6 to 10.....	S2
3. CVs of compounds 8 to 10.....	S3
4. Computational details .....	S4
5. Equilibrium structures.....	S4
6. Comparison between computed and observed absorption spectra.....	S6
7. References.....	S12
8. <sup>1</sup> H, <sup>13</sup> C NMR and MALDI-TOF Spectra of compounds 6 to 10.....	S13

## 1. Materials and Methods:

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in deuterated solvents on a Bruker ADVANCE 300 NMR Spectrometer and a Bruker ADVANCE 400 NMR Spectrometer. <sup>1</sup>H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. Mass spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX III Mass Spectrometer, and High resolution mass spectra (HRMS) were determined on Bruker Apex IV Fourier Transform Mass Spectrometer.

Absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer in a 1-cm quartz cell. All fluorescence spectra are corrected. The fluorescence quantum yields were determined by optical dilute method ( $A < 0.05$ ) using Cresyl Violet ( $\phi_f = 0.54$  in Methanol)<sup>1</sup> as reference for **9** and **10**, and parent PDI as reference for **8**.

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. Starting materials tetrabromo-TDI (compound **4**) and hexabromo-QDI (compound **5**) are prepared by using the procedures reported by references and patents.<sup>2</sup> 2-(tributylstannyl)thiophene and compound **3** were synthesized according to literature.<sup>3,4</sup>

## 2. Synthesis and characterization of compounds 6 to 10

### Compound 8:

A mixture of compound **3** (600mg, 1equiv), 2-(tributylstannyl) thiophene (775mg, 3equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (40mg, 5%equiv) in 100 ml toluene was stirred at 110°C for 24 h under nitrogen. After cooling to room temperature, the solvent was evaporated under reduced pressure. The crude product was put into acetone and refluxed for 3 h, filtered, and the residue was washed by mixture solvents of CH<sub>2</sub>Cl<sub>2</sub> and hexane (1:1) to yield the orange solid product (450mg, 75 %).

<sup>1</sup>H NMR (1,1,2,2-Tetrachloroethane-D<sub>2</sub>, 300 MHz, 320 K):  $\delta$  = 10.43 (s, 2H), 10.27 (s, 2H), 8.88 (d, 2H), 8.31 (d, 2H), 7.61 (t, 2H), 7.48 (d, 4H), 3.03-2.96 (q, 4H), 1.29 (d, 24H). MS (MALDI-TOF):  $m/z$  ( $M$ ) = 870.1 (calcd for C<sub>56</sub>H<sub>42</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>: 871.1). HRMS: calcd for C<sub>56</sub>H<sub>43</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub><sup>+</sup>: [M+H]<sup>+</sup>: 871.2659; found 871.2645.

### Compound 6:

A mixture of compound **4** (1g, 1equiv), 2-(tributylstannyl)thiophene (3.2g, 10equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (100mg, 10% equiv) in 100 ml toluene was stirred at 110°C for 24 h under nitrogen. After cooling to room temperature, the reaction mixture was poured into water and the product was extracted with diethyl ether. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 1:1) to yield the green solid product (738mg, 73 %).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298K):  $\delta$  = 8.64 (s, 4H), 7.84 (s, 4H), 7.49 (t, 2H), 7.40 (d, 4H), 7.35 (d, 4H), 7.27 (d, 4H), 7.15 (t, 4H), 2.79-2.73 (m, 4H), 1.19 (d, 24H). MS (MALDI-TOF):  $m/z$  ( $M$ ) = 1162.0 (calcd for C<sub>74</sub>H<sub>54</sub>N<sub>2</sub>O<sub>4</sub>S<sub>4</sub>: 1163.5). HRMS: calcd for C<sub>74</sub>H<sub>55</sub>N<sub>2</sub>O<sub>4</sub>S<sub>4</sub><sup>+</sup>: [M+H]<sup>+</sup>: 1163.3039; found 1163.3030.

### Compound 9:

A solution of FeCl<sub>3</sub> (416mg, 10equiv) in 2 ml nitromethane was added dropwise to a stirred solution of compound **6** (300mg, 1equiv) in 10 ml CH<sub>2</sub>Cl<sub>2</sub>. The reaction mixture turned immediately red. The reaction vessel was flushed with argon. After stirring for 20 min at room

temperature, the solution was poured into water and the product was extracted with  $\text{CH}_2\text{Cl}_2$ . The solvent was evaporated under reduced pressure, and the crude product was washed with methanol until the filtrate was colorless to yield the red solid product (274mg, 92%).

$^1\text{H}$  NMR (1,1,2,2-Tetrachloroethane- $\text{D}_2$ , 300 MHz, 360 K):  $\delta$  = 10.40 (s, 4H), 8.65 (s, 4H), 8.14 (d, 4H), 7.65 (t, 2H), 7.53 (d, 4H), 3.18 (s, 4H), 1.40 (s, 24H). MS (MALDI-TOF):  $m/z$  ( $M$ ) = 1154.3 (calcd for  $\text{C}_{74}\text{H}_{46}\text{N}_2\text{O}_4\text{S}_4$ : 1155.5). HRMS:  $\text{C}_{74}\text{H}_{47}\text{N}_2\text{O}_4\text{S}_4^+$ :  $[\text{M}+\text{H}]^+$ : 1155.2413; found 1155.2427.

#### Compound 7:

A mixture of compound 5 (1g, 1equiv), 2-(tributylstannyl)thiophene (3.9g, 15equiv),  $\text{Pd}(\text{PPh}_3)_4$  (81mg, 10%equiv) in 100 ml toluene was stirred at  $110^\circ\text{C}$  for 24 h under nitrogen. After cooling to room temperature, the reaction mixture was poured into water and the product was extracted with diethyl ether. The solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether/ $\text{CH}_2\text{Cl}_2$ , 1:2) to yield the gray solid product (365mg, 36 %).

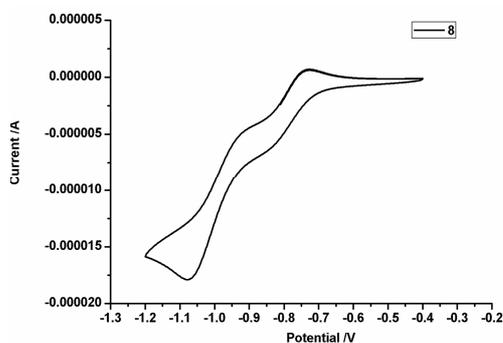
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298K):  $\delta$  = 8.67 (d, 4H), 8.29 (s, 2H), 7.76 (q, 4H), 7.57 (d, 2H), 7.47 (t, 2H), 7.36-7.26 (m, 14H), 7.12 (t, 2H), 7.06 (t, 2H), 6.83 (d, 2H), 2.81-2.74 (m, 4H), 1.19 (d, 24H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, 298K):  $\delta$  = 163.7, 163.6, 145.7, 145.4, 145.3, 144.9, 136.2, 136.1, 135.8, 134.9, 132.2, 132.1, 131.3, 130.8, 130.7, 130.4, 129.5, 129.4, 128.7, 128.6, 128.5, 128.4, 128.3, 127.7, 127.6, 127.5, 127.4, 127.3, 126.9, 126.7, 124.0, 120.4, 120.2, 29.2, 24.0, 1.0. MS (MALDI-TOF):  $m/z$  ( $M$ ) = 1450.1 (calcd for  $\text{C}_{92}\text{H}_{62}\text{N}_2\text{O}_4\text{S}_6$ : 1451.9). HRMS: calcd for  $\text{C}_{92}\text{H}_{63}\text{N}_2\text{O}_4\text{S}_6^+$ :  $[\text{M}+\text{H}]^+$ : 1451.3107; found 1451.3078.

#### Compound 10:

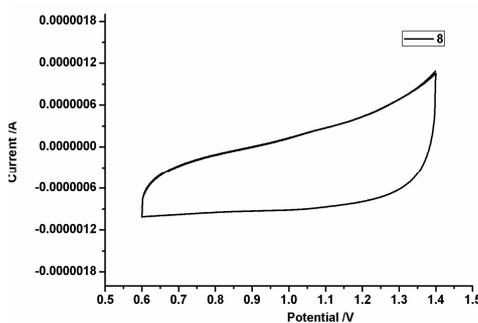
A solution of  $\text{FeCl}_3$  (666mg, 20equiv) in 2 ml nitromethane was added dropwise to a stirred solution of compound 7 (300mg, 1equiv) in 10 ml  $\text{CH}_2\text{Cl}_2$ . The reaction was stirred with argon. After stirring for 20 min at room temperature, 1 ml methanol was added to the solution. The solvent was evaporated under reduced pressure, and the crude product was washed with methanol until the filtrate was colorless to yield the gray-black solid product (268mg, 90%).

$^1\text{H}$  NMR (1,1,2,2-Tetrachloroethane- $\text{D}_2$ , 300 MHz, 380 K):  $\delta$  = 10.53 (s, 4H), 9.45 (d, 4H), 8.58 (s, 2H), 8.31 (s, 4H), 7.89 (s, 2H), 7.66 (t, 2H), 7.54 (d, 4H), 3.16 (s, 4H), 1.39 (s, 24H). MS (MALDI-TOF):  $m/z$  ( $M$ ) = 1439.6 (calcd for  $\text{C}_{92}\text{H}_{50}\text{N}_2\text{O}_4\text{S}_6$ : 1439.8). HRMS: calcd for  $\text{C}_{92}\text{H}_{51}\text{N}_2\text{O}_4\text{S}_6^+$ :  $[\text{M}+\text{H}]^+$ : 1439.2168; found 1439.2200.

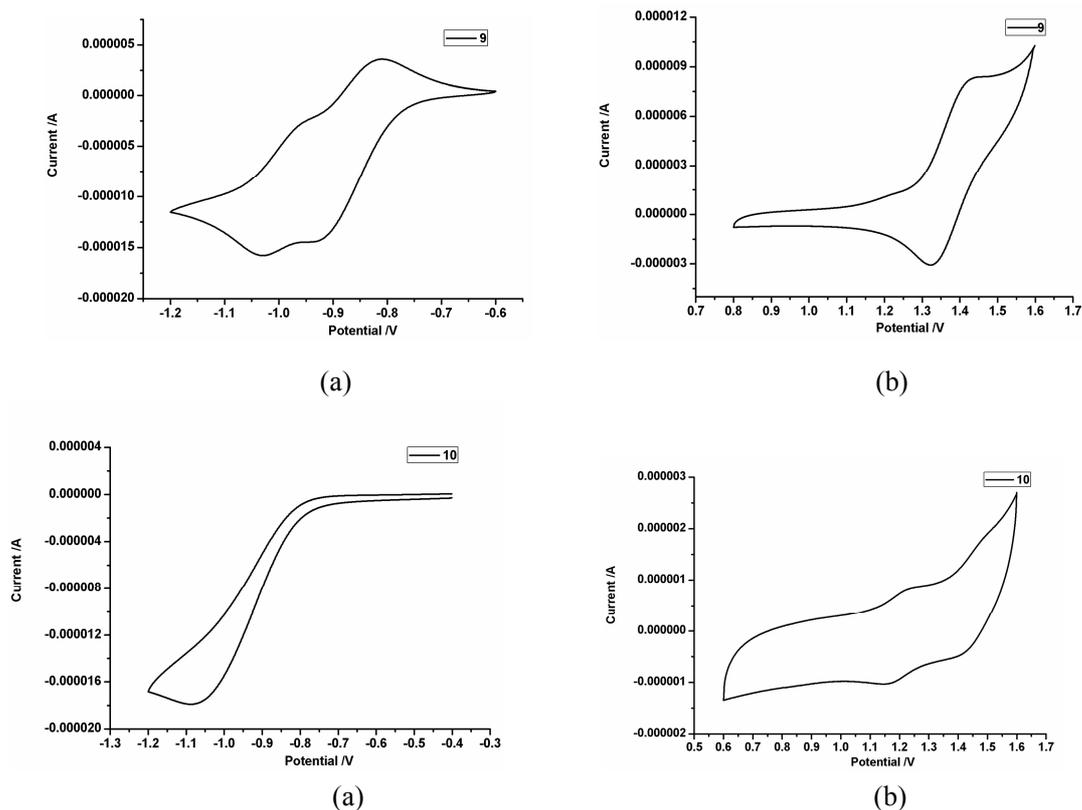
### 3. CVs of compounds 8 to 10



(a)



(b)



**Figure S1:** Reductive (a) and oxidative (b) cyclic voltammogram of compounds **8**, **9** and **10** in  $\text{CH}_2\text{Cl}_2$ . Scan rate=0.1V/s (electrolyte, 0.1M TBAPF<sub>6</sub>).

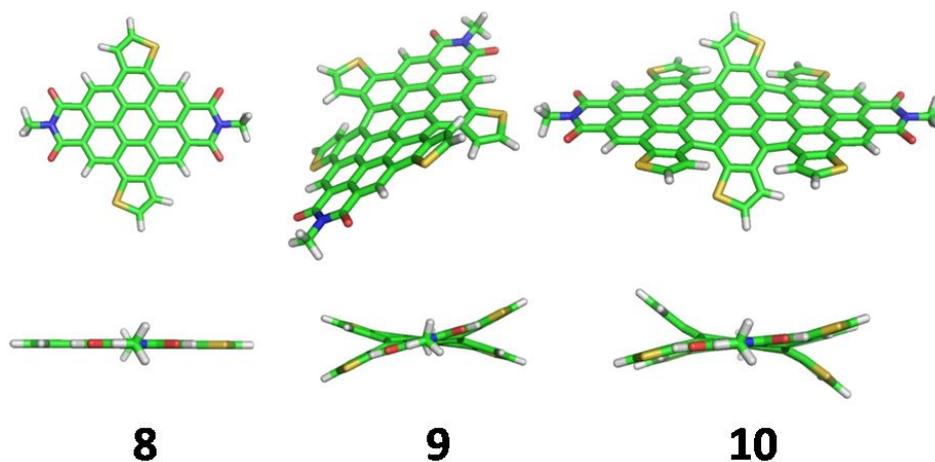
#### 4. Computational details:

Atomic structures of models for compounds **6**, **7**, **8**, **9** and **10** along with those of the reference compounds perylene-, terrylene-, quaterrylene- and coronene-diimide (PDI, TDI, QDI and CDI), featuring methyl substituents at the imide position, were optimized with density functional theory (DFT) calculations using the B3LYP hybrid functional<sup>5</sup> with the 6-31G\* basis set. Molecular orbital shapes and energies discussed in the text are those calculated at the lowest energy optimized structures. Orbital pictures were prepared with Molekel 4.3 visual software.<sup>6</sup> Electronic excitation energies and oscillation strengths were computed for the thirty lowest singlet excited electronic states of the investigated compounds with time dependent (TD) DFT calculations run at the optimized geometry. In plotting computed electronic spectra, a Lorentzian linewidth of 0.1 eV was superimposed to each computed intensity to facilitate the comparison with experimental spectra. The computed spectra did not include the vibronic structure associated with electronic bands and as a result they show a reduced number of bands compared with the experimental spectra. All quantum-chemical calculations were performed with the Gaussian09 package.<sup>7</sup>

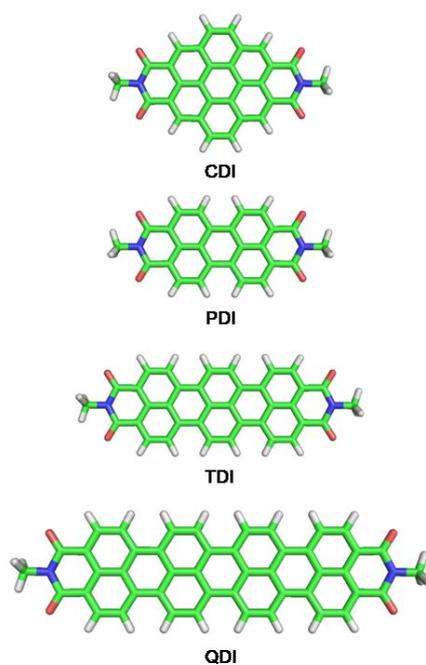
#### 5. Equilibrium structures:

The computed equilibrium structures of all the most stable isomers of the investigated compounds are collected in Figures S2-S4. While only one conformer exists for **8**, several conformation exist

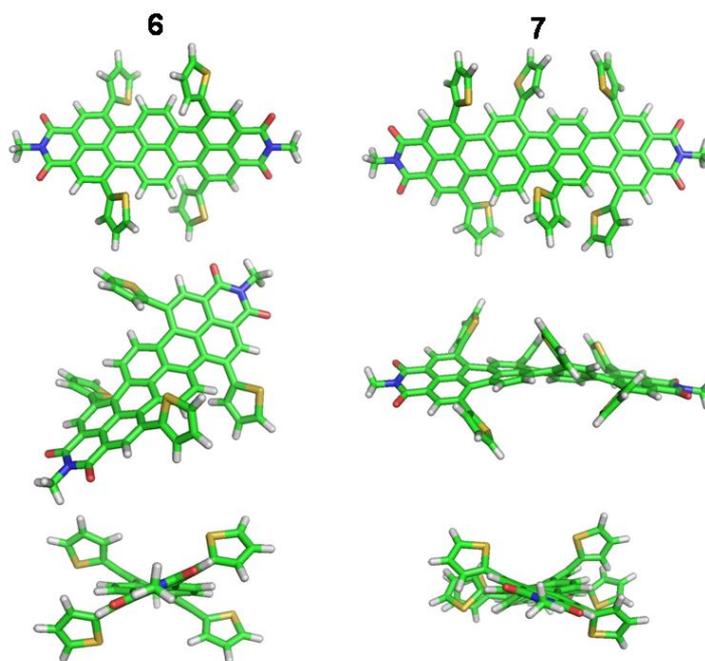
for most of the remaining compounds, especially for **6** and **7**. The spectroscopic properties were simulated, in this work, considering only the most stable conformer for each species.



**Figure S2.** The B3LYP/6-31G\* computed lowest energy structures of **8**, **9** and **10**.



**Figure S3.** The B3LYP/6-31G\* equilibrium structures of models of **CDI**, **PDI**, **TDI** and **QDI**.



**Figure S4.** The B3LYP/6-31G\* equilibrium structures of the lowest energy structures of models of **6** and **7**.

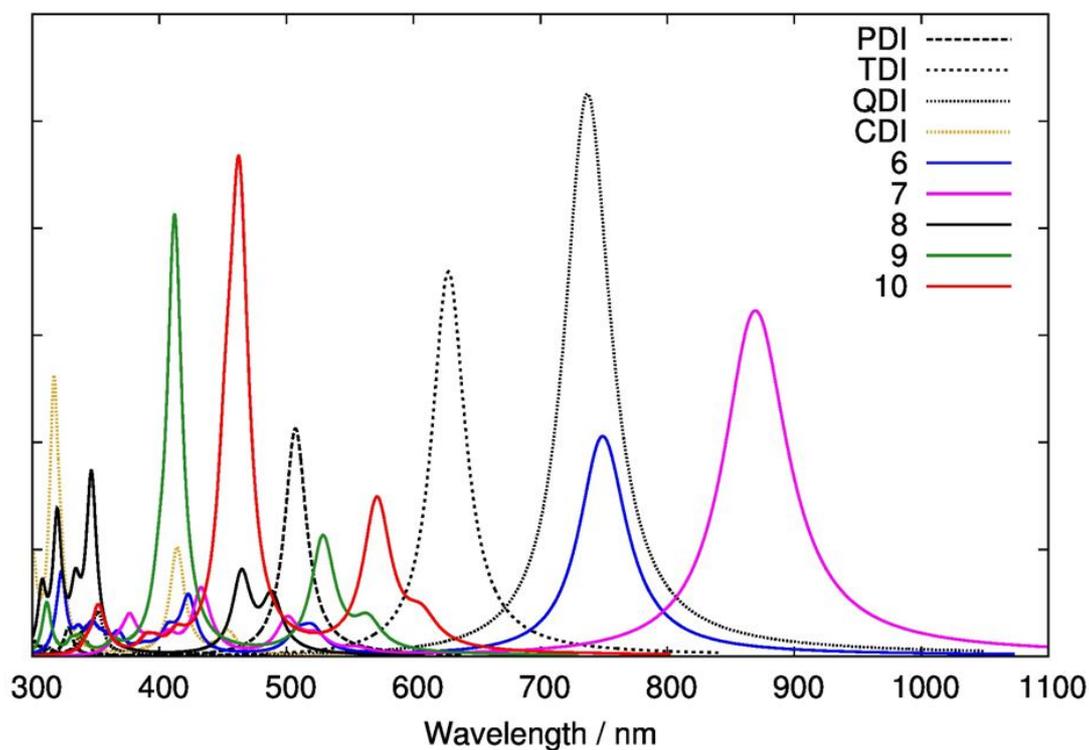
## 6. Comparison between computed and observed absorption spectra:

To assist the interpretation of the experimental absorption spectra, the electronic transitions were calculated at TD-B3LYP/6-31G\* level for all the systems whose geometry was previously optimized. The orbital nature of the low lying electronic transitions was identified for all the species. The computed spectra of **6**, **7**, **8**, **9** and **10** are compared with the observed absorption spectra in Figure 2 while in Figure S5 the same computed spectra are compared with those computed for PDI, TDI, QDI and CDI. The TD-B3LYP calculated bands agree very closely with the most prominent observed features in the experimental spectra and the smaller number of bands in the computed spectra is due to the neglect of vibronic structures associated with the electronic transitions. A summary of computed electronic structure data for the systems investigated is collected in Tables S1-S3.

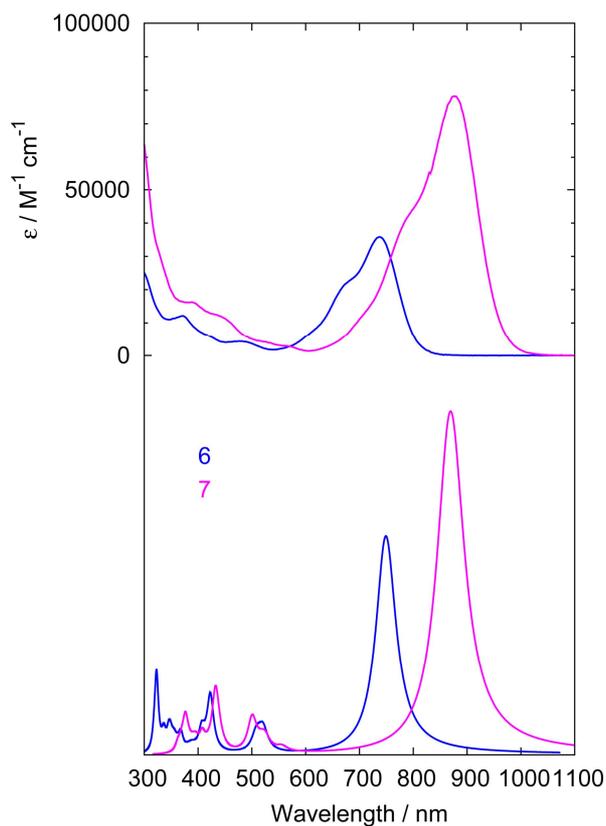
The computed spectra of **6** and **7** show a low energy band in close agreement with the observation. This band is dominated by the HOMO→LUMO transition as in the case of the parent compounds TDI and QDI. A scheme of orbital levels and shapes are presented in Figure S7, from which it is evident that the frontier orbitals of TDI and **6** have the same parentage, as well those of QDI and **7**. The higher energy of the HOMOs of **6** and **7** compared to TDI and QDI, due to the electron-rich character of the thiophene substituents, implies a bathochromic shift of the lowest excitation energy, as observed. The bathochromic shift is computed to be 0.32 eV for **6** (with respect to TDI) and 0.25 eV for **7** (with respect to QDI). These values compare quite closely with the observed shifts of 0.23 eV and 0.21 eV, respectively.

In contrast with most rylene-diimide derivatives, the spectra of **8**, **9** and **10** show the presence of two low-lying electronic transitions both associated with some vibronic structure, as shown in Figure S8 for **8**. The nature of these transitions is clarified by considering **8** and its related system CDI, which is also known to display two low lying electronic transitions.

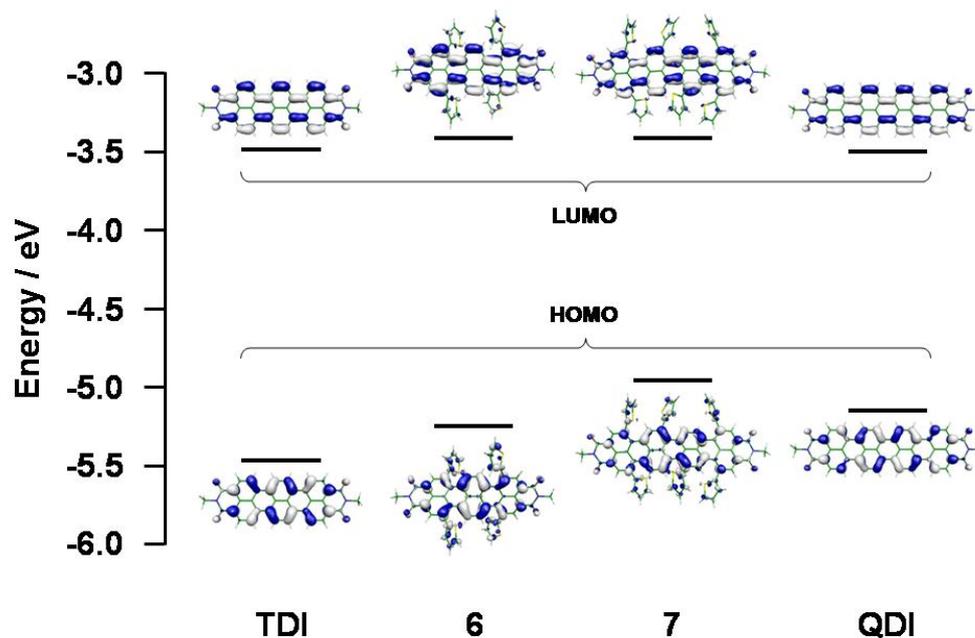
Inspection of the orbital nature of the two electronic excitations shows indeed a close parentage between **8** and CDI, as detailed in Figure S9. The more extended  $\pi$  system (via fused thiophenes) in **8**, compared to CDI, does not change the nature of the low-lying electronic transitions but shifts the HOMO orbital to higher energies such that the absorption in **8** is bathochromically shifted compared to CDI.



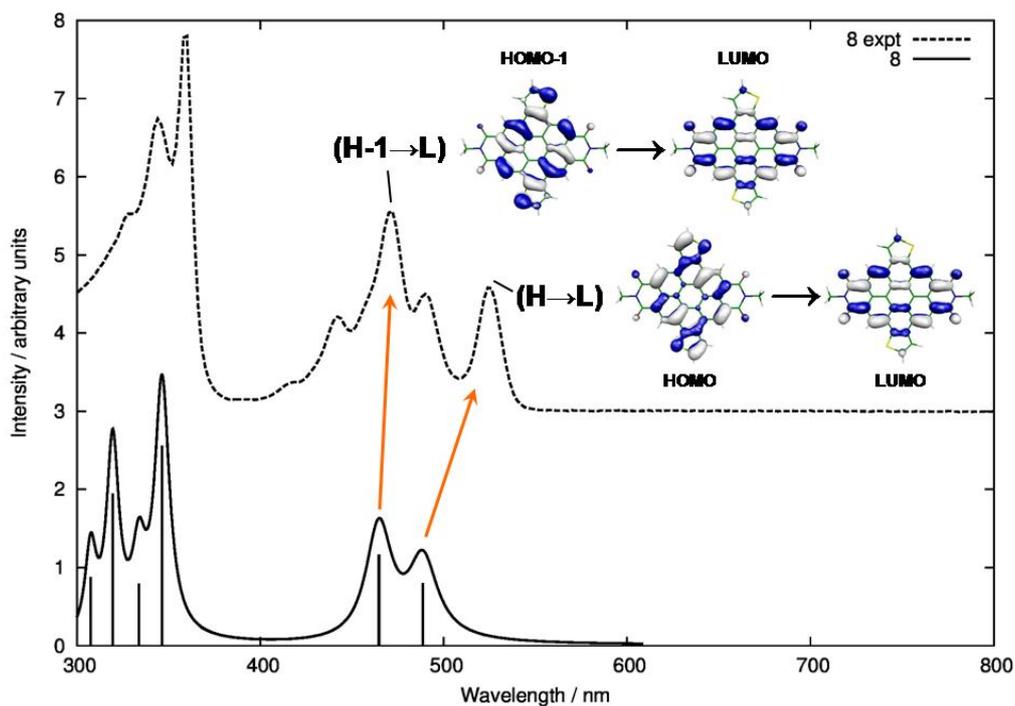
**Figure S5.** Comparison between computed UV-Vis absorption spectra (TD-B3LYP/6-31G\*) of all the model systems investigated.



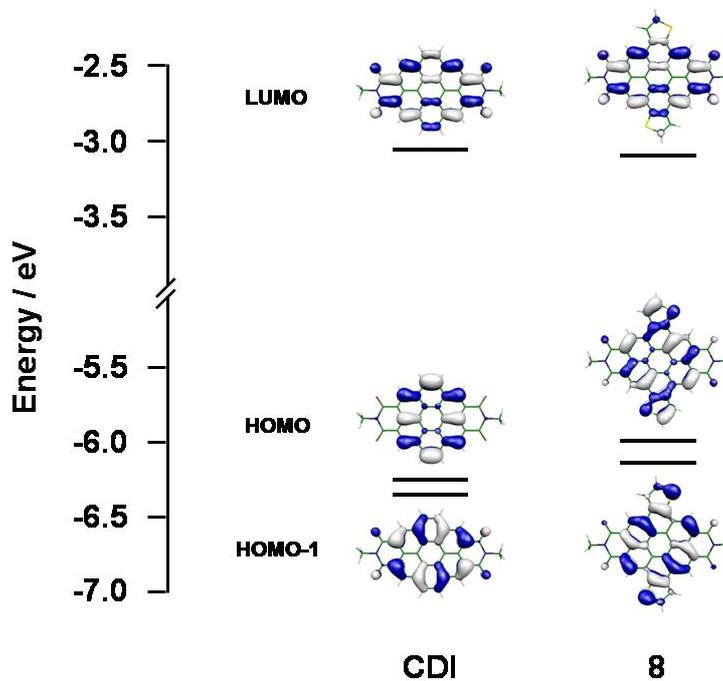
**Figure S6.** Comparison between TD-B3LYP/6-31G\* computed (bottom) and observed (top) UV/vis absorption spectra of **6** (blue line), **7** (magenta line) in CHCl<sub>3</sub> ( $1 \times 10^{-5}$  M) at room temperature.



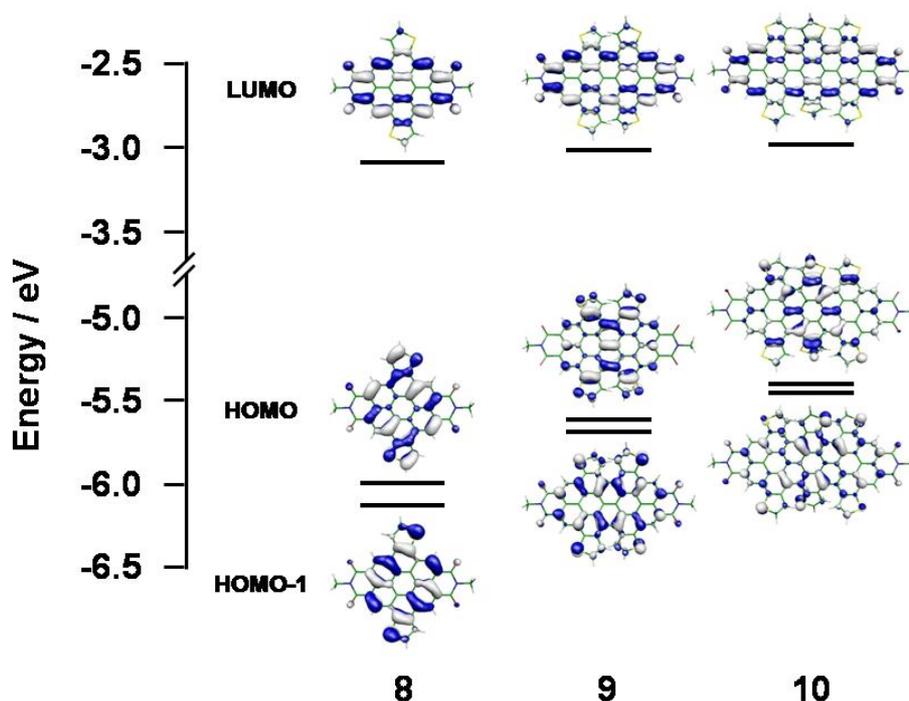
**Figure S7.** Energies and shapes of B3LYP/6-31G\* frontier  $\pi$  orbitals of model TDI, QDI, **6** and **7** showing the dominant orbital parentage.



**Figure S8.** Comparison between computed and observed UV-Vis absorption spectra and analysis of the two low-lying electronic excitations of **8**. Bottom: the TD B3LYP/6-31G\* calculated absorption spectrum; Top: experimental UV-Vis absorption spectra of **8** in CHCl<sub>3</sub>.



**Figure S9.** Energies and shapes of B3LYP/6-31G\* frontier  $\pi$  orbitals of model CDI and **8**, showing the dominant orbital parentage.



**Figure S10.** Energies and shapes of B3LYP/6-31G\* frontier  $\pi$  orbitals of model **8**, **9** and **10**, showing the dominant orbital parentage.

**Table S1:** B3LYP/6-31G\* absolute energies, relative energies, optical gaps (lowest allowed electronic transitions from TDDFT B3LYP/6-31G\* calculations), and the second most important electronic transition in absorption spectra.

	Absolute Energy (a.u.)	$E(S_0 \rightarrow S_1)$ (eV, [nm]) and $f$	$E(S_0 \rightarrow S_n)$ (eV, [nm]) and $f$
PDI	-1409.74686651	2.45 [507] (0.668)	-
TDI	-1793.26500631	1.98 [628] (1.129)	-
QDI	-2176.78282608	1.68 [737] (1.650)	-
CDI	-1562.23394192	2.73 [454] (0.065)	3.00 [414] (0.315)
<b>8</b>	-2511.04439146	2.54 [489] (0.160)	2.67 [465] (0.233)
<b>6</b>	-4000.46288251	1.66 [749] (0.645)	2.38 [521] (0.067)
<b>9</b>	-3995.81723477	2.20 [564] (0.086)	2.34 [529] (0.339)
<b>7</b>	-5487.58211465	1.43 [869] (1.014)	2.23 [555] (0.015)
<b>10</b>	-5480.59397088	2.04 [606] (0.083)	2.17 [571] (0.441)

**Table S2:** MO energies of  $\pi$  orbitals and HOMO-LUMO gaps of the investigated compounds. From B3LYP/6-31G\* calculations at optimized geometries.

	HOMO-2 (eV)	HOMO-1 (eV)	HOMO (eV)	$\Delta E(H-L)$ (eV) Transport gap	LUMO (eV)	LUMO+1 (eV)
PDI	-7.32	-7.32	-6.00	2.54	-3.46	-1.87
TDI	-7.17	-6.74	-5.48	1.99	-3.49	-2.28
QDI	-6.95	-6.18	-5.15	1.65	-3.50	-2.53
CDI	-7.32	-6.36	-6.25	3.18	-3.07	-2.16
<b>8</b>	-6.79	-6.13	-5.99	2.89	-3.10	-2.08
<b>6</b>	-6.30	-6.24	-5.23	1.82	-3.41	-2.30
<b>9</b>	-6.38	-5.69	-5.63	2.60	-3.02	-2.35
<b>7</b>	-6.19	-5.84	-4.95	1.54	-3.41	-2.54
<b>10</b>	-5.94	-5.47	-5.41	2.43	-2.98	-2.44

**Table S3:** Orbital nature of the lowest allowed electronic transitions of the investigated systems.

	$E(S_0 \rightarrow S_1)$ (eV) and $f$	Exp Optical gap (eV) [nm]	Dominant electronic excitation	$E(S_0 \rightarrow S_n)$ (eV) and $f$	Dominant electronic excitation
PDI	2.45 (0.668)	2.35 [527]	(H $\rightarrow$ L)	-	-
TDI	1.98 (1.129)	1.91 [650] <sup>a</sup>	(H $\rightarrow$ L)	-	-
QDI	1.68 (1.650)	1.63 [760] <sup>b</sup>	(H $\rightarrow$ L)	-	-
CDI	2.73 (0.065)	2.43 [511] <sup>c</sup>	(H $\rightarrow$ L)	3.00 (0.315)	(H-1 $\rightarrow$ L)
<b>8</b>	2.54 (0.160)	2.37 [524]	(H $\rightarrow$ L)	2.67 (0.233)	(H-1 $\rightarrow$ L)
<b>6</b>	1.66 (0.645)	1.68 [738]	(H $\rightarrow$ L)	2.38 (0.067)	(H-1 $\rightarrow$ L)
<b>9</b>	2.20 (0.086)	2.07 [600]	(H $\rightarrow$ L)	2.34 (0.339)	(H-1 $\rightarrow$ L)
<b>7</b>	1.43 (1.014)	1.42 [876]	(H $\rightarrow$ L)	2.23 (0.015)	(H $\rightarrow$ L+1) (H-1 $\rightarrow$ L)
<b>10</b>	2.04 (0.083)	1.96 [634]	(H $\rightarrow$ L)	2.17 (0.441)	(H-1 $\rightarrow$ L)

<sup>a</sup> From ref. [8].

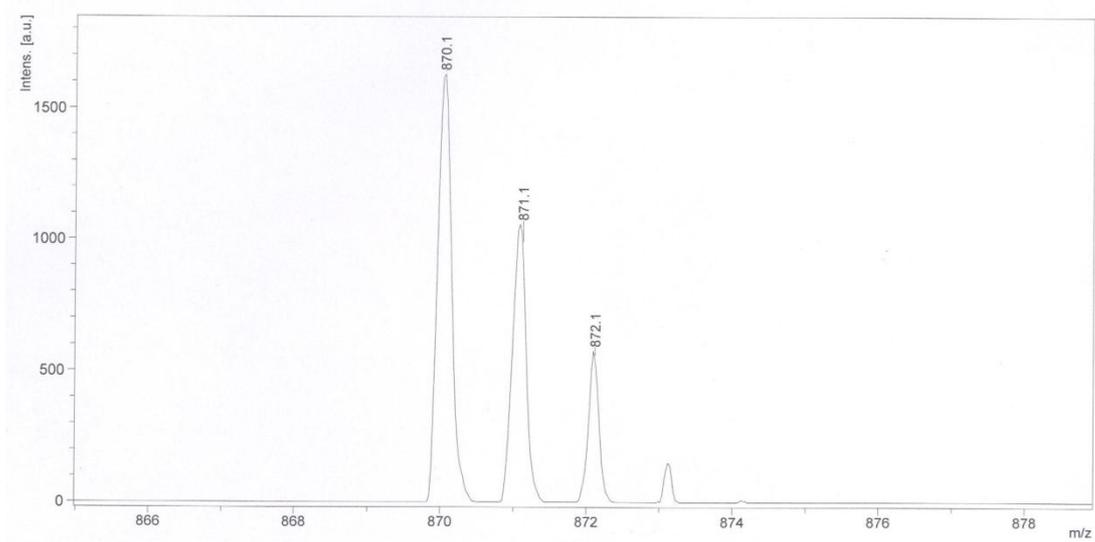
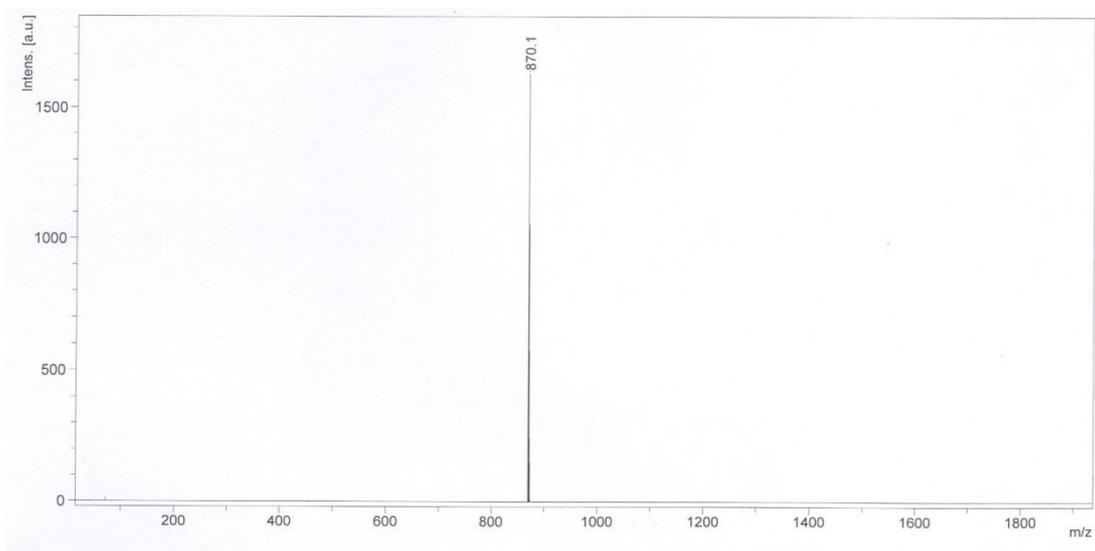
<sup>b</sup> From ref. [9].

<sup>c</sup> From ref. [10].

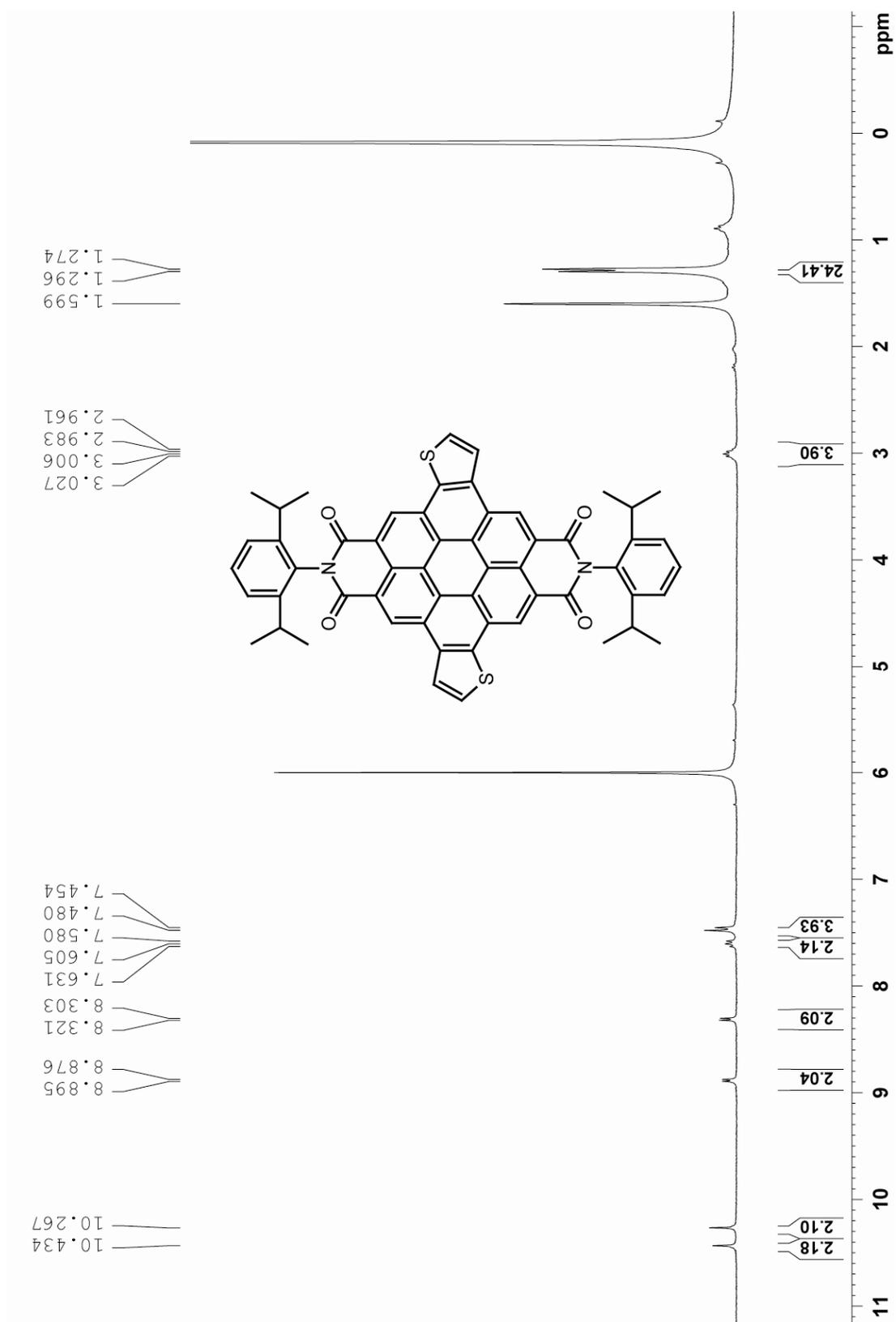
## References:

- (1) Lakowicz J. R. *Principles of Fluorescence Spectroscopy*, 2nd ed., Kluwer Academic/Plenum, New York, 1999, 52.
- (2) (a) T. Weil, E. Reuther, C. Beer and K. Müllen, *Chem. Eur. J.*, 2004, **10**, 1398; (b) Y. Avlasevich, S. Müller, P. Erk and K. Müllen, *Chem. Eur. J.*, 2007, **13**, 6555; (c) J. Qu, M. Koenemann, W. Helfer, K. Müllen, J. Romeis and A. Bohm, US2007155968; (d) M. Koenemann and N. G. Pschirer, US2008058526.
- (3) Ando, S.; Nishida, J.; Fujiwara, E.; Tada, H.; Inoue, Y.; Tokito, S.; Yamashita, Y. *Chem. Mater.* 2005, **17**, 1261.
- (4) Jiang, W.; Li, Y.; Yue, W.; Zhen Y.; Qu, J.; Wang, Z. *Org. Lett.* **2010**, *12*, 228.
- (5) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098-3100; (b) Lee, C.; Yang, W.; Parr, G. G. *Phys. Rev. B* **1988**, *37*, 785-789.
- (6) Molekel, version 4.3, <http://www.cscs.ch/molekel/>; Portmann, S.; Lüthi, H. P. *Chimia* **2000**, *54*, 766.
- (7) Frisch, M. J.; et al. *Gaussian 09*, revision A.02; Gaussian, Inc., Wallingford CT, 2009.
- (8) F. O. Holtrup, G. R. J. Müller, H. Quante, S. D. Feyter, F. C. D. Schryver and K. Müllen, *Chem. Eur. J.*, 1997, **3**, 219
- (9) Y. Geerts, H. Quante, H. Platz, R. Mahrt, M. Hopmeier, A. Bohm and K. Müllen, *J. Mater. Chem.*, 1998, **8**, 2357.
- (10) Rohr, U., Schlichting, P., Böhm, A.; Gross, M.; Meerholz, K.; Bräuchle, C., Müllen, K. *Angew. Chem. Int. Ed.* 1998, **37**, 1434.

MALDI-TOF mass spectrum of **8**

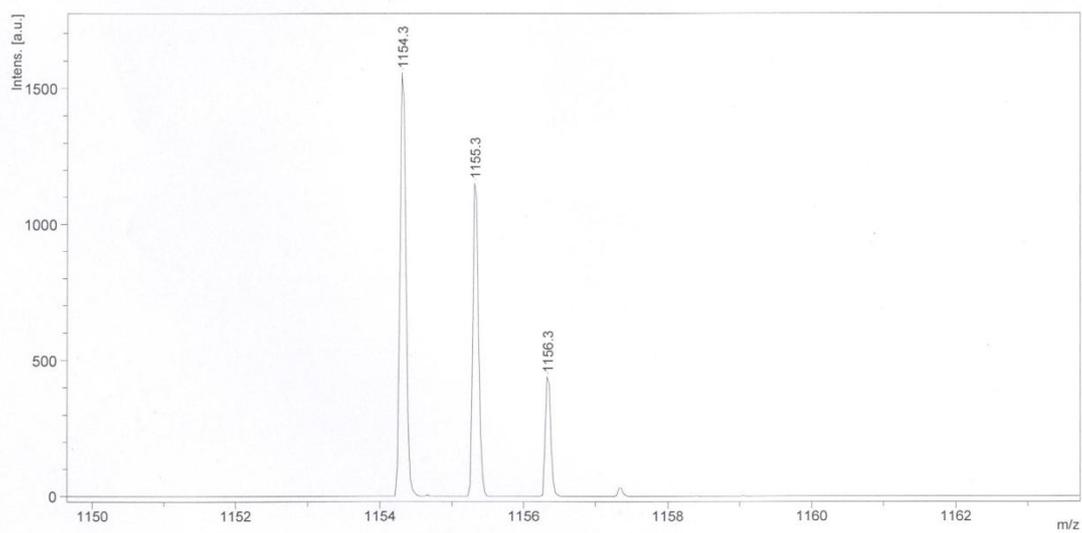
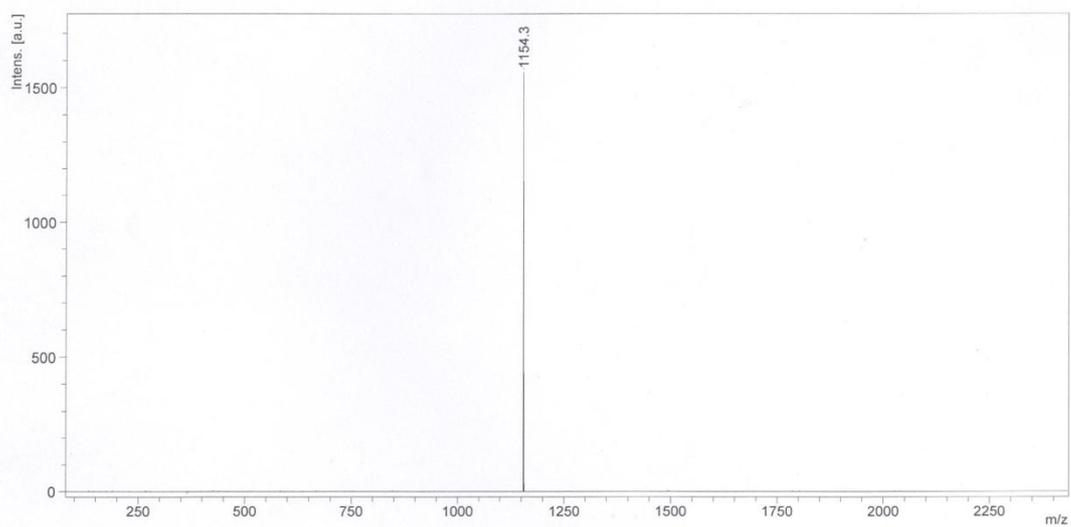


$^1\text{H}$  NMR spectrum of **8** in 1,1,2,2-Tetrachloroethane- $\text{D}_2$  (320 K)

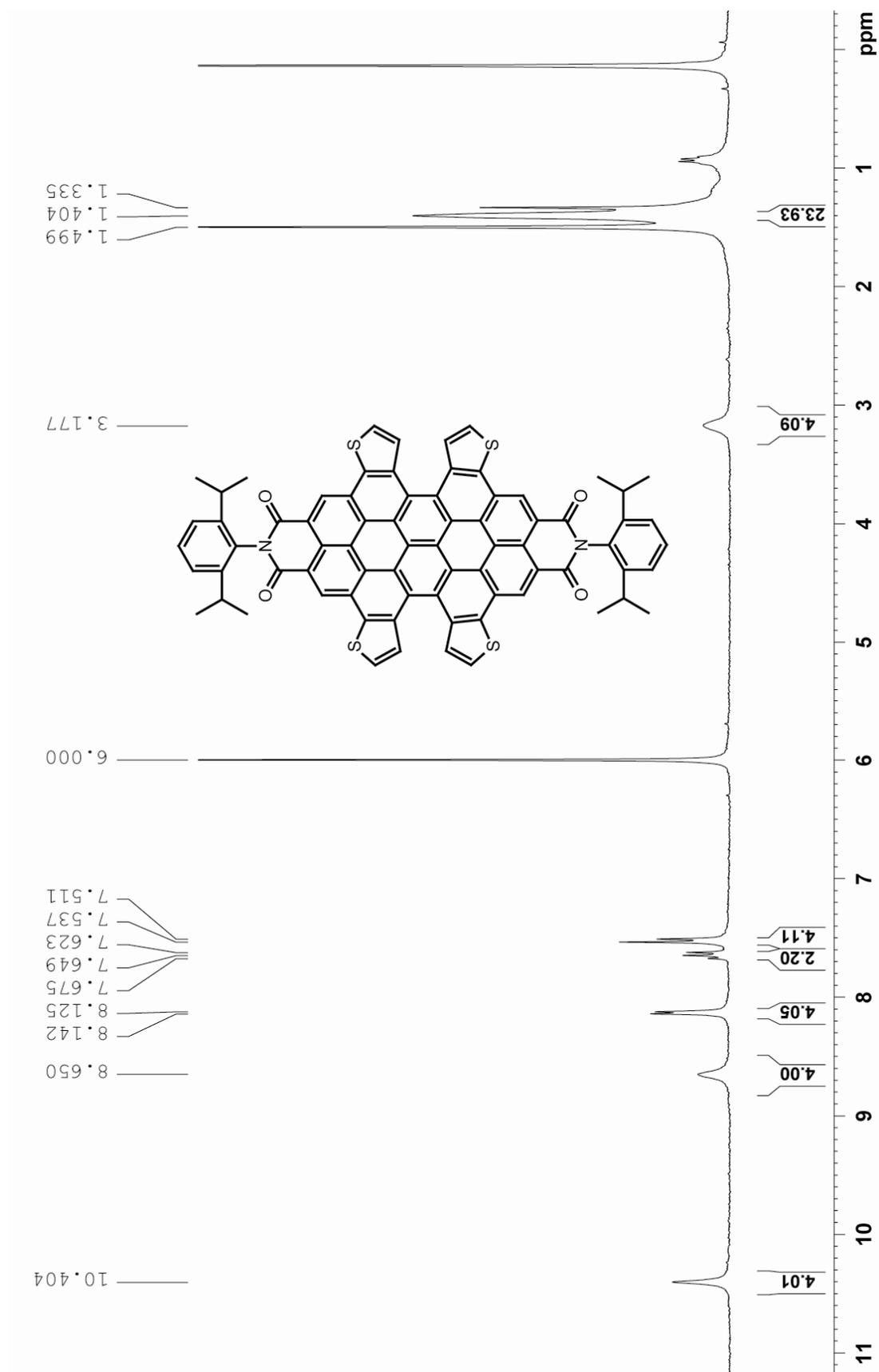




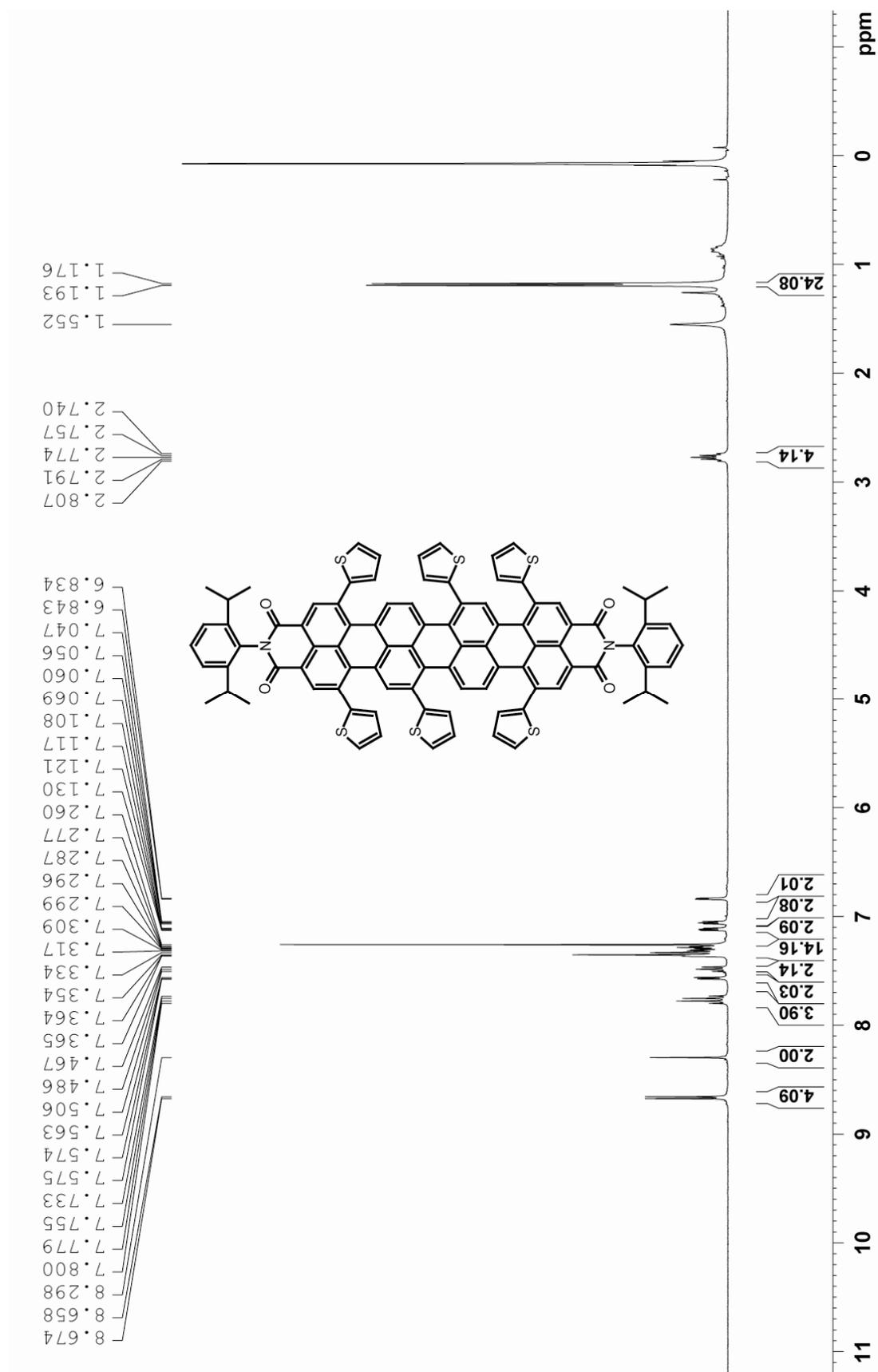
MALDI-TOF mass spectrum of **9**



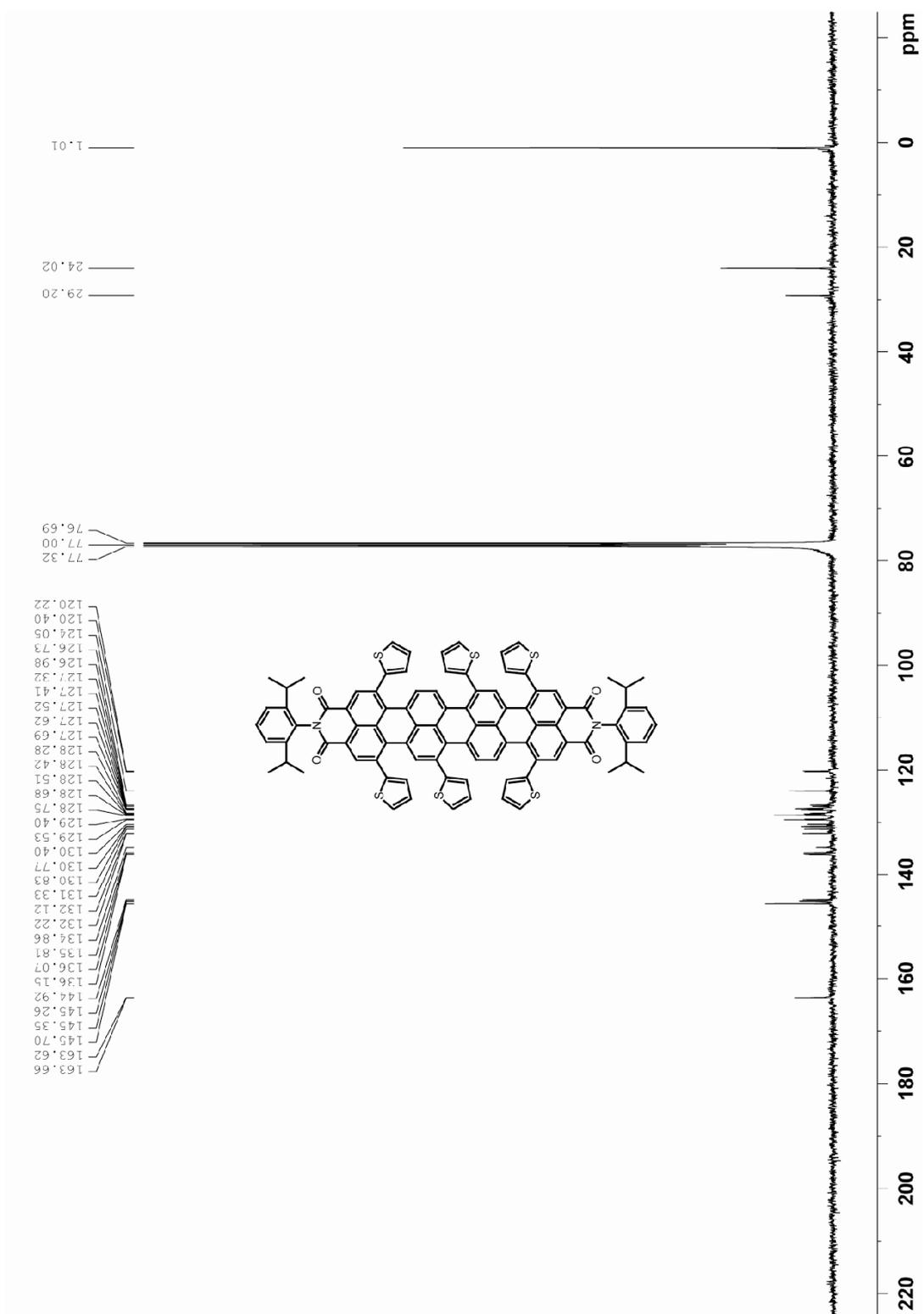
$^1\text{H}$  NMR spectrum of **9** in 1,1,2,2-Tetrachloroethane- $\text{D}_2$  (360 K)



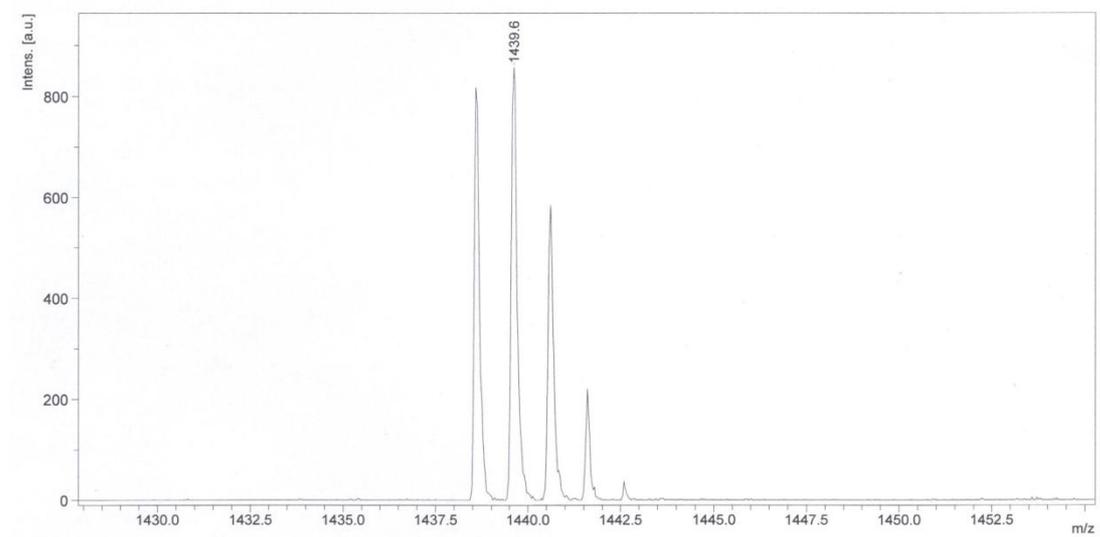
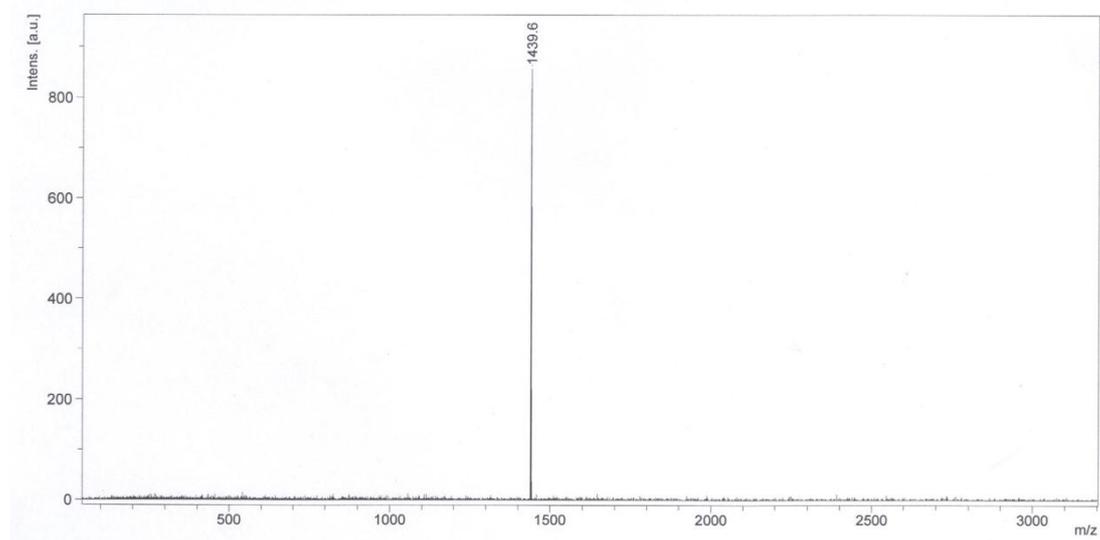
$^1\text{H}$  NMR spectrum of 7 in  $\text{CDCl}_3$



$^{13}\text{C}$  NMR spectrum of **7** in  $\text{CDCl}_3$



MALDI-TOF mass spectrum of **10**



$^1\text{H}$  NMR spectrum of **10** in 1,1,2,2-Tetrachloroethane- $\text{D}_2$  (380 K)

