Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

The effect of the molecular structures of dicyanomethylene compounds on their supramolecular assembly, photophysical and electrochemical properties

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Supporting Information

Fourier transform infrared and ^{1}H and ^{13}C NMR spectra of the synthesized compounds

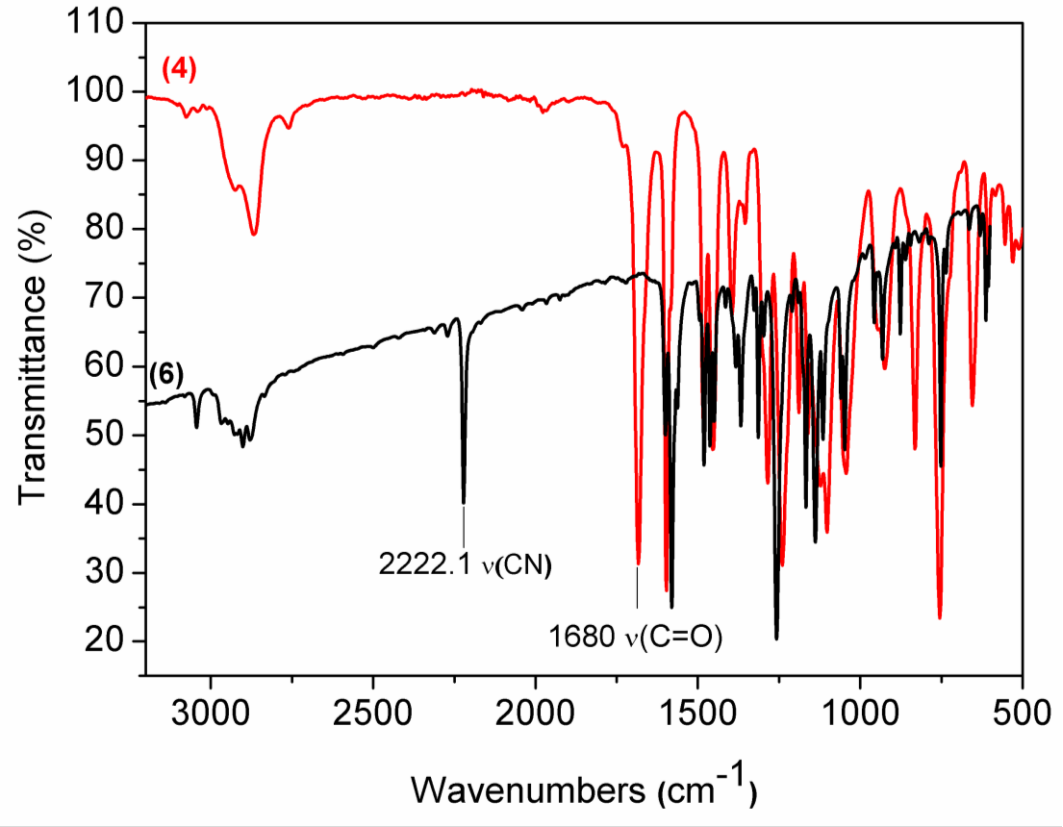

Fig. S1 IR spectra of compounds (**3**) and (**5**).

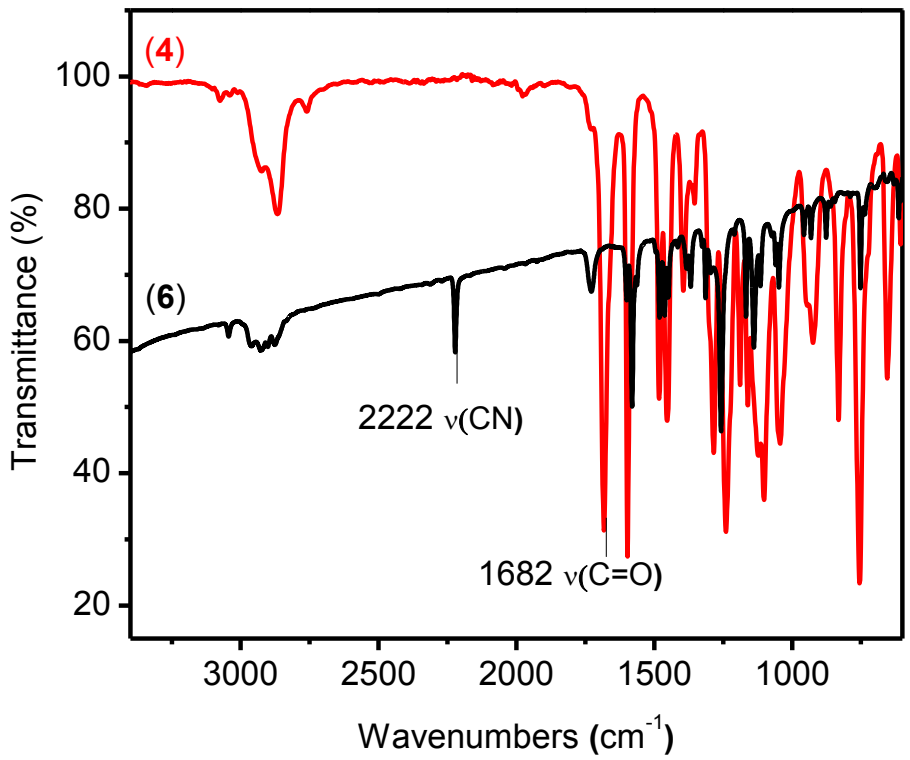

Fig. S2 IR spectra of compounds (**4**) and (**6**).

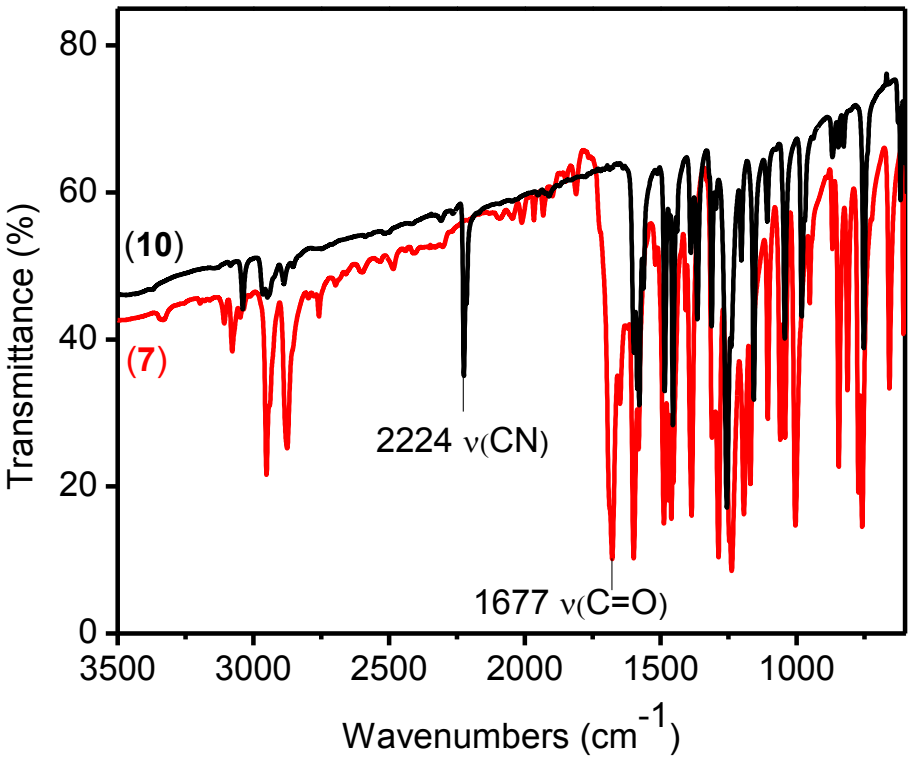

Fig. S3 IR spectra of compounds (**7**) and (**10**).

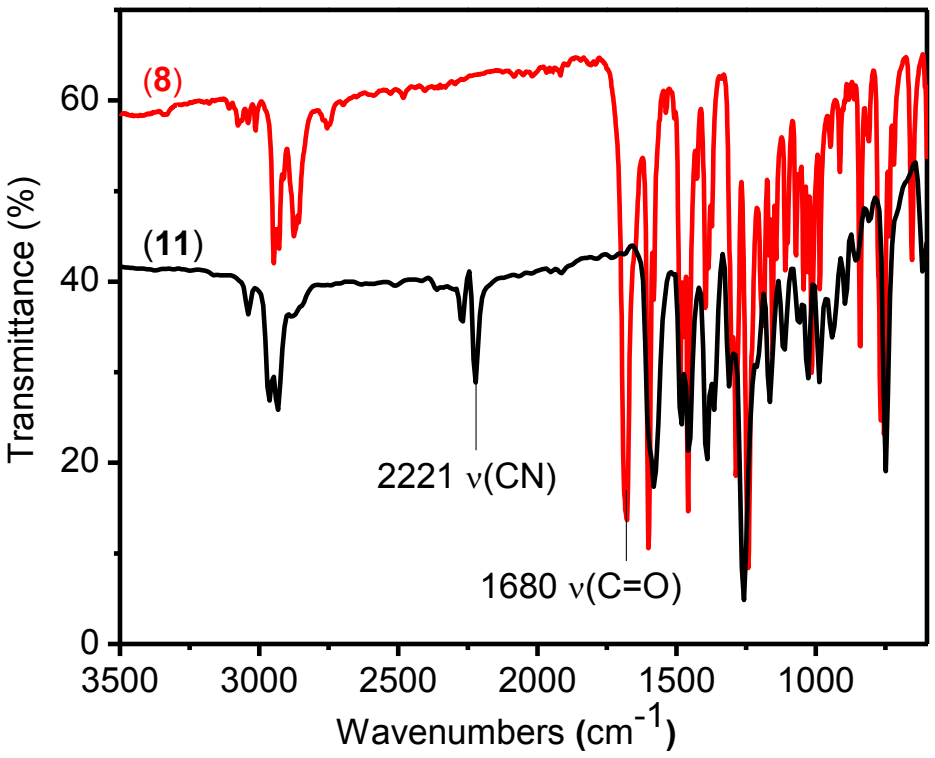

Fig. S4 IR spectra of compounds (**8**) and (**11**).

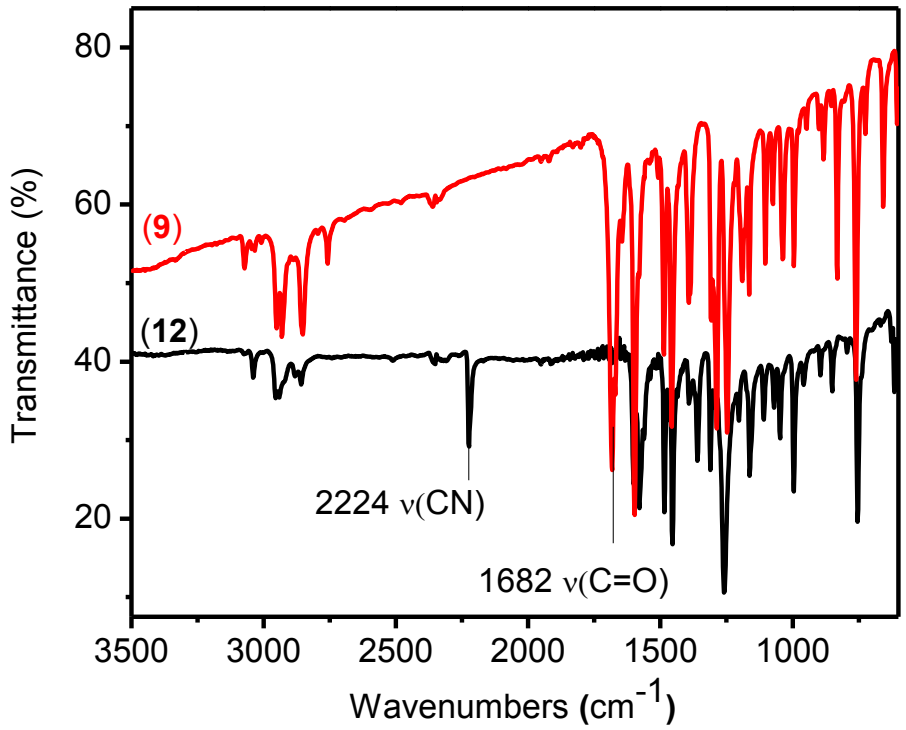

Fig. S5 IR spectra of compounds (**9**) and (**12**).

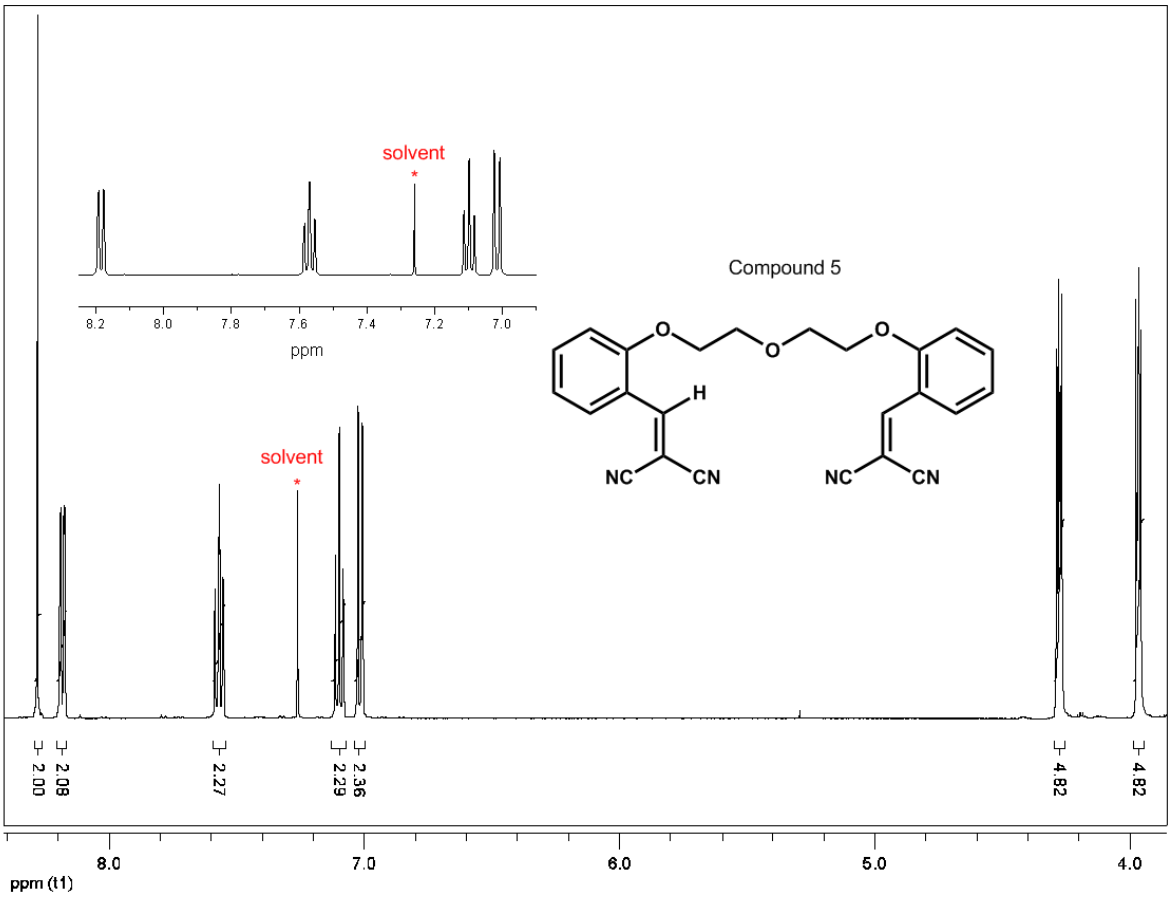

Fig. S6 ^{1}H NMR spectrum of compound (**5**) (500 MHz, 298K, $CDCl_3$).

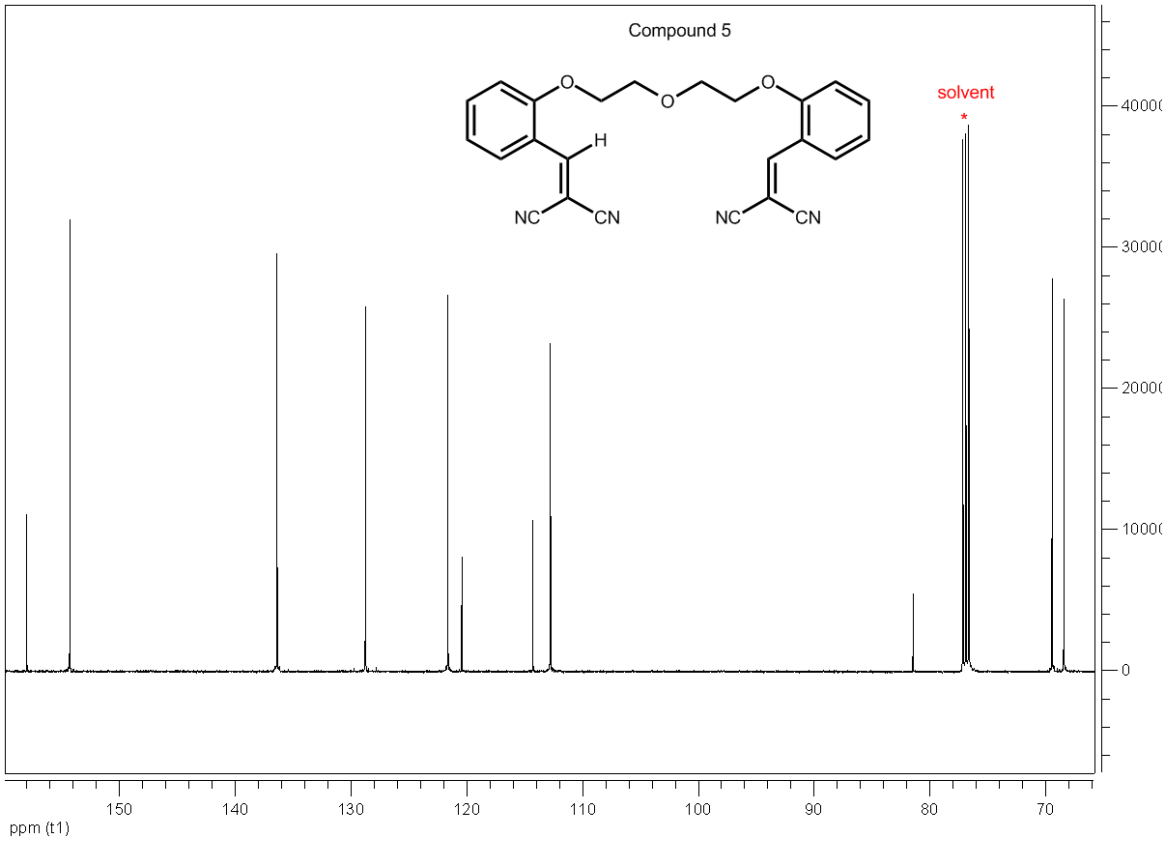

Fig. S7 ^{13}C NMR spectrum of compound (**5**) (125 MHz, 298K, $CDCl_3$).

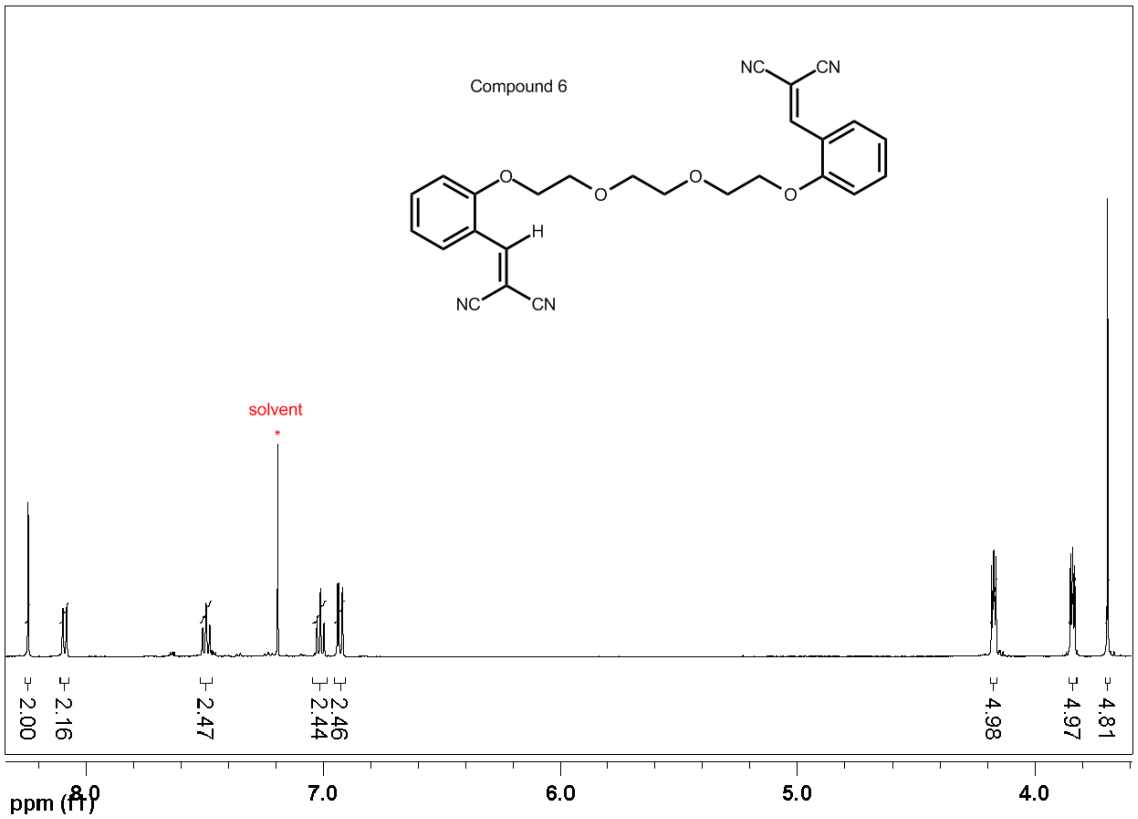

Fig. S8 ^{1}H NMR spectrum of compound (**6**) (500 MHz, 298K, $CDCl_3$).

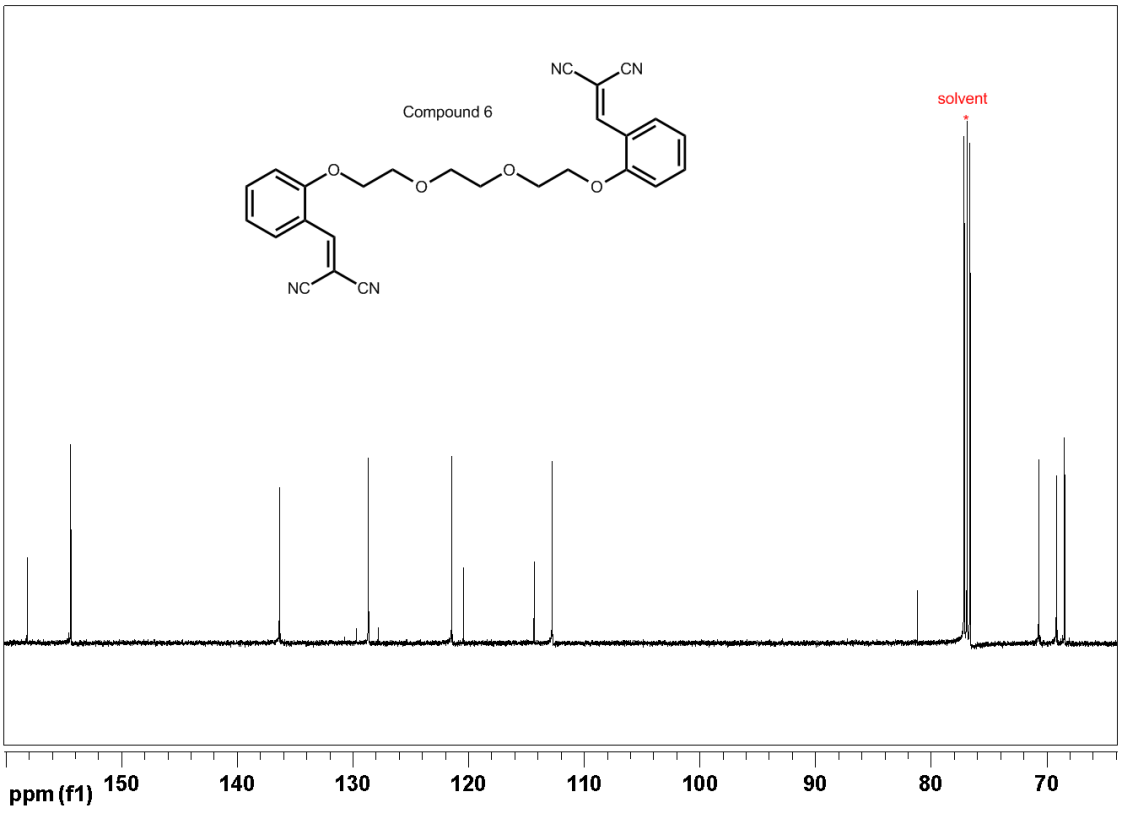

Fig. S9 ^{13}C NMR spectrum of compound (**6**) (125 MHz, 298K, $CDCl_3$).

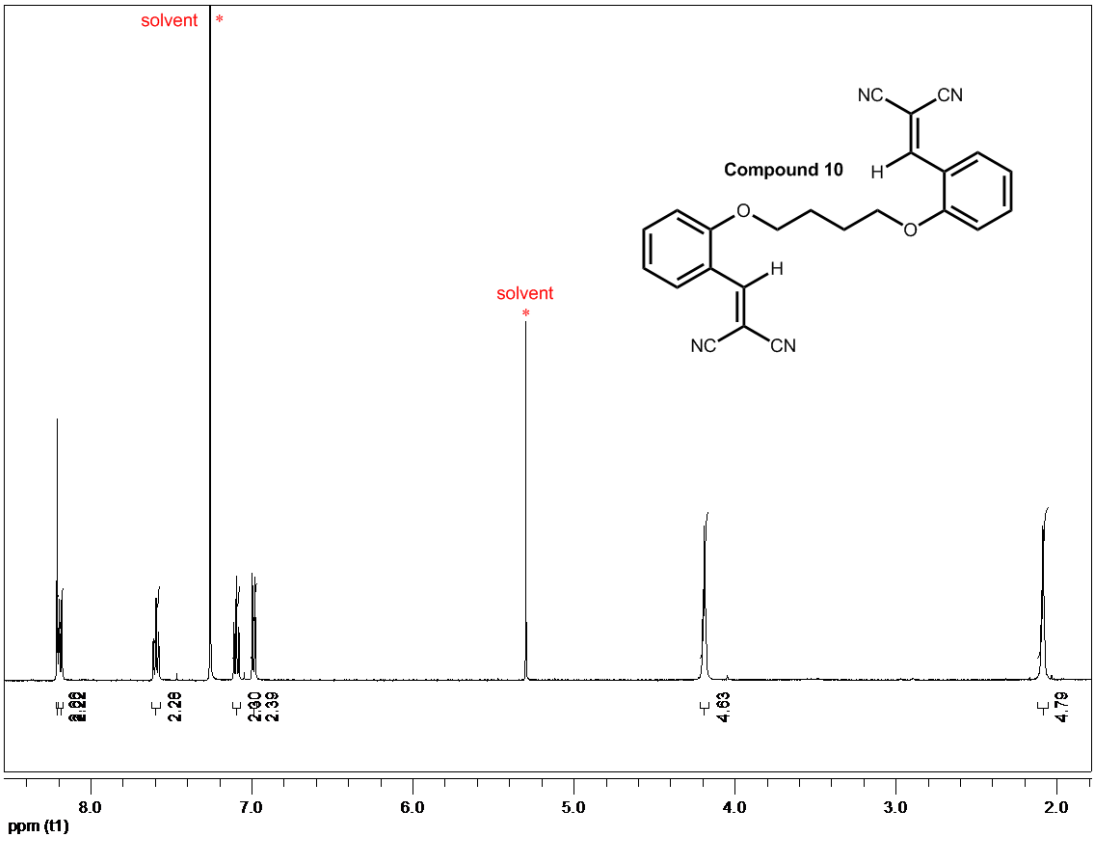

Fig. S10 ^{1}H NMR spectrum of compound (**10**) (500 MHz, 298K, $CDCl_3$).

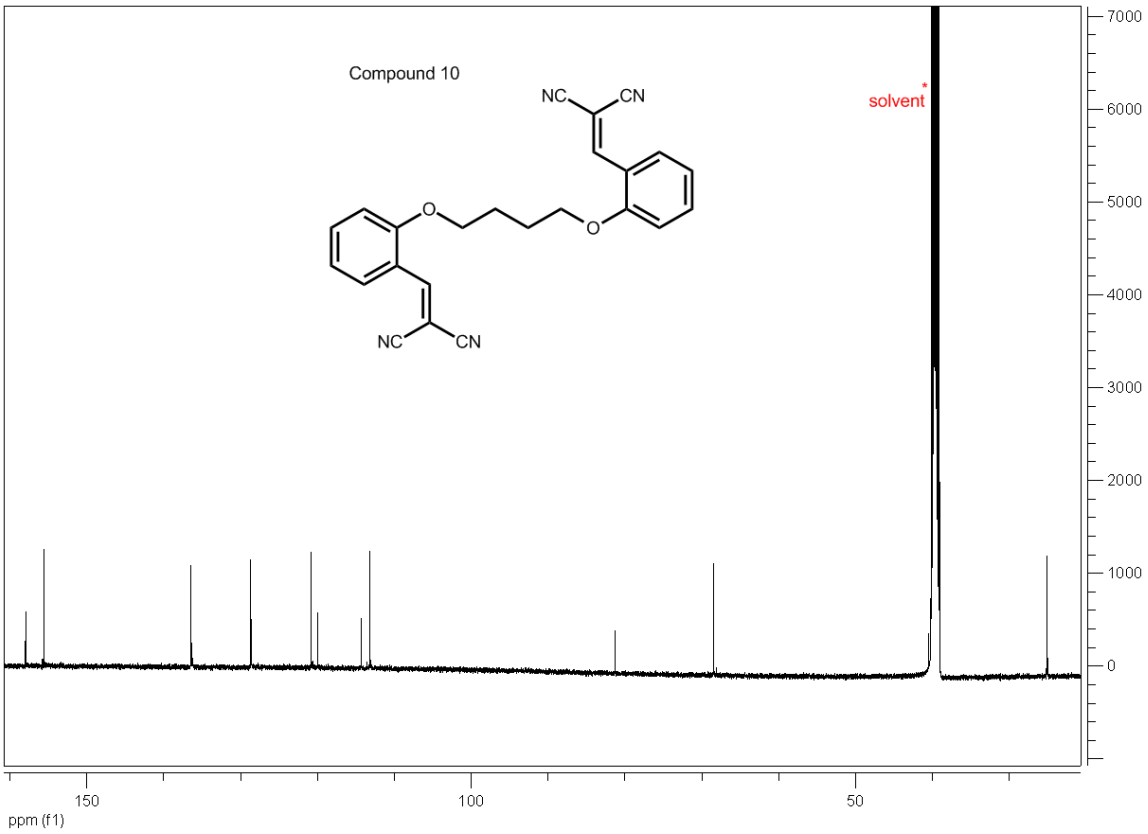

Fig. S11 ^{13}C NMR spectrum of compound (**10**) (125 MHz, 298K, DMSO).

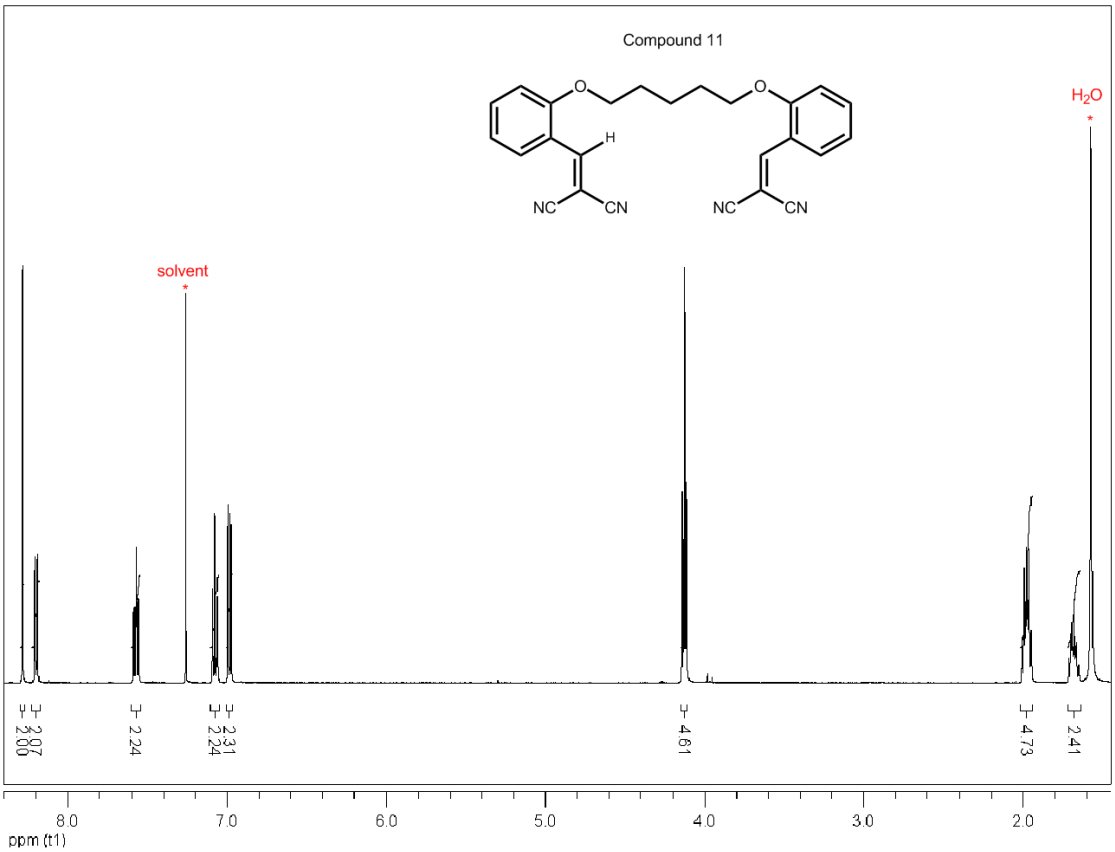

Fig. S12 ^{1}H NMR spectrum of compound (**11**) (500 MHz, 298K, CD_3Cl).

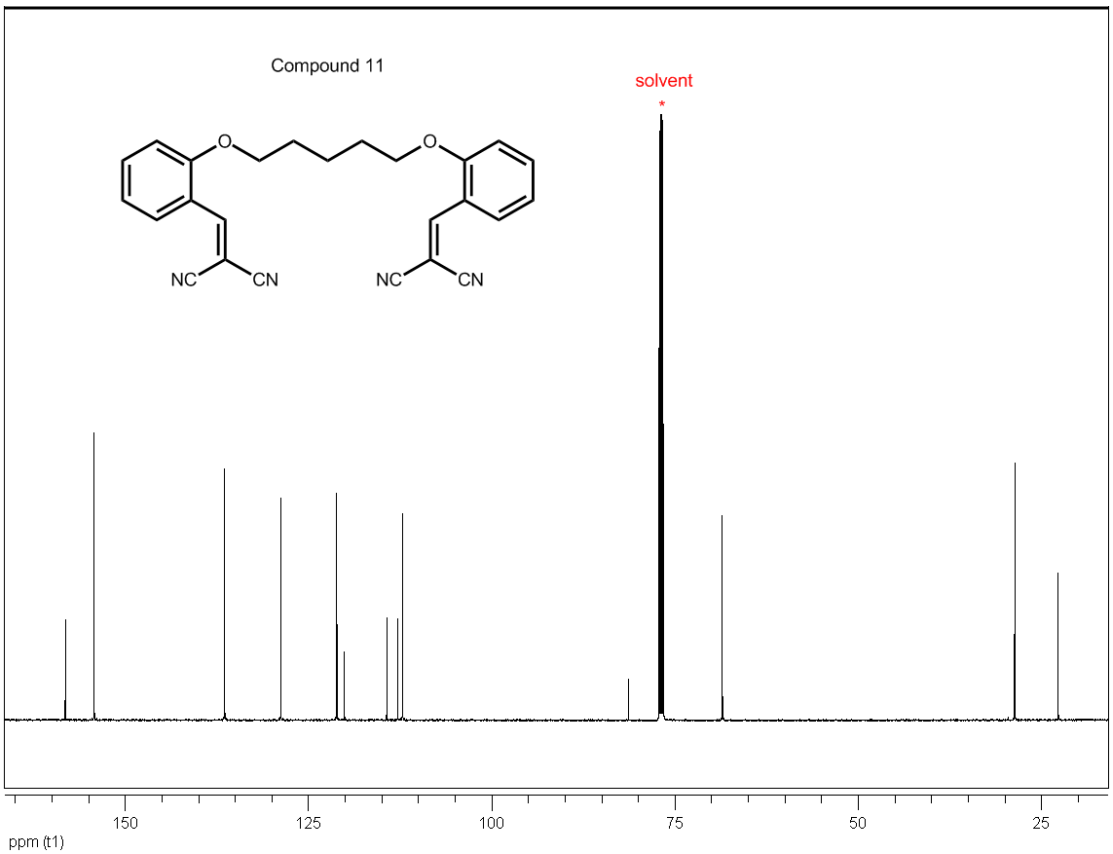

Fig. S13 ^{13}C NMR spectrum of compound (**11**) (125 MHz, 298K, $CDCl_3$).

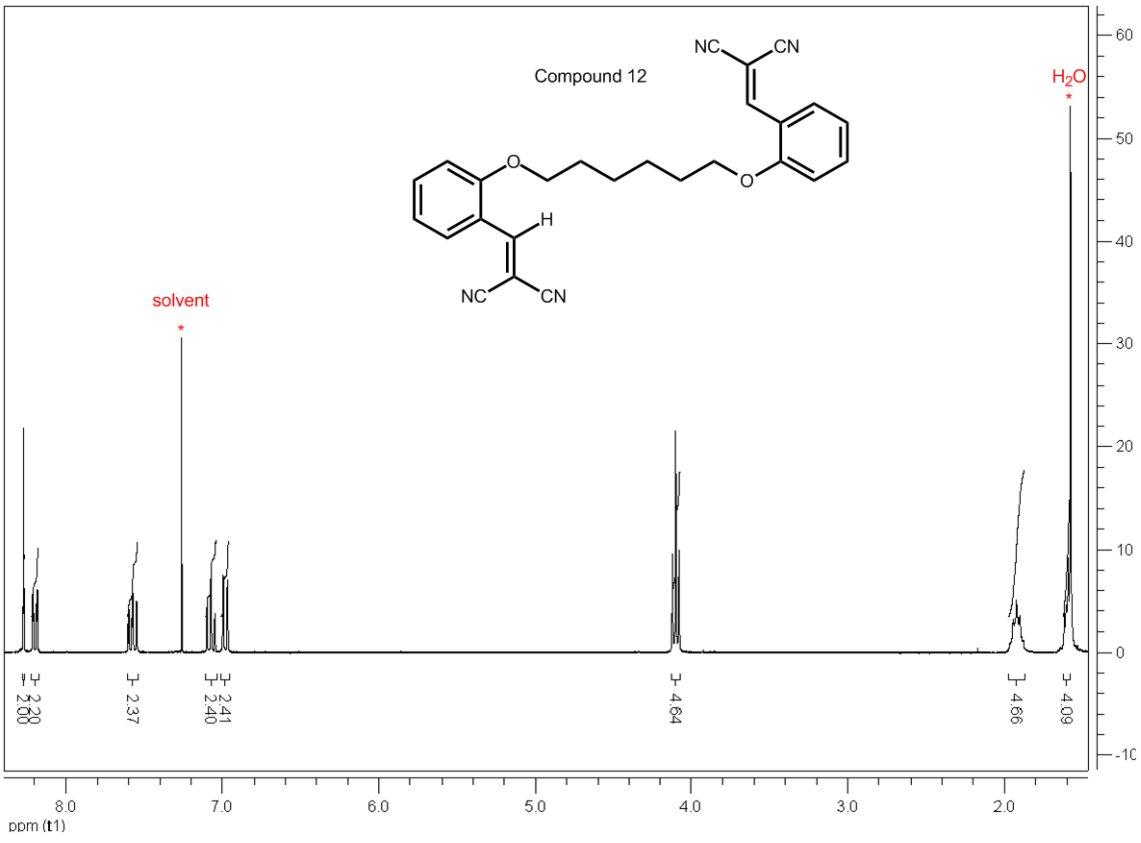

Fig. S14 ^{1}H NMR spectrum of compound (**12**) (500 MHz, 298K, $CDCl_3$).

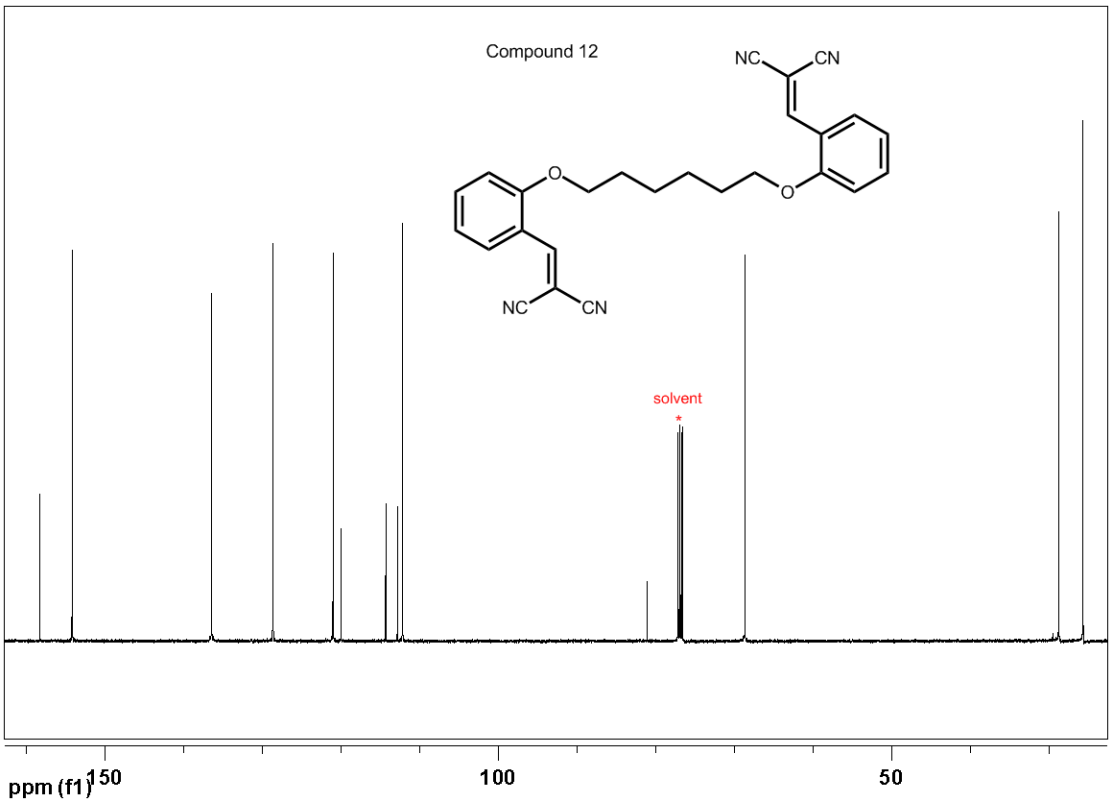

Fig. S15 ^{13}C NMR spectrum of compound (**12**) (125 MHz, 298K, $CDCl_3$).

Structural analysis

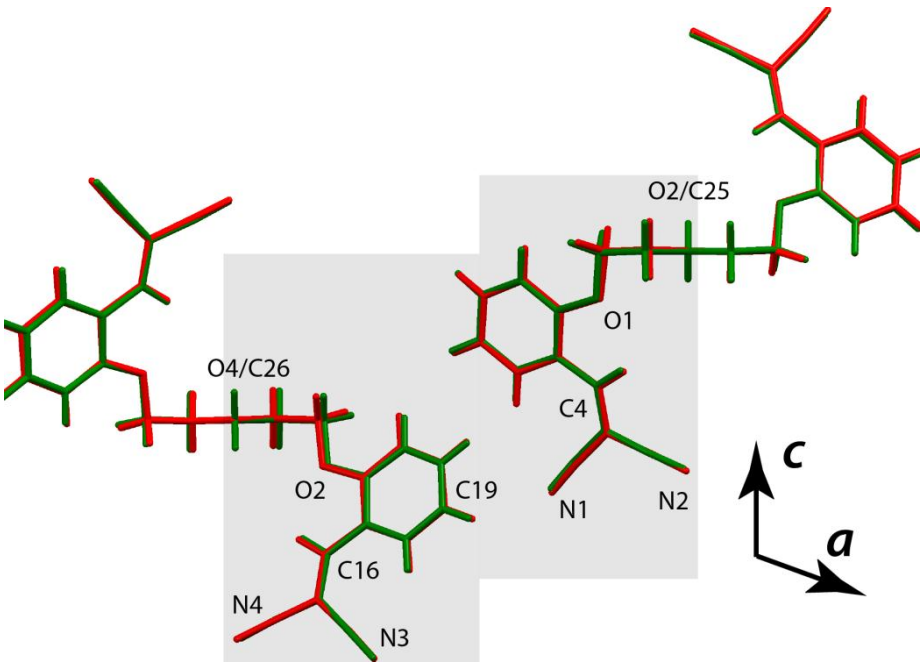

Fig. S16 Overlay of the structures of compounds **5** (red) and **11** (green) in which the grey area highlights the asymmetric unit. Relevant atoms for the structure packing are indicated.

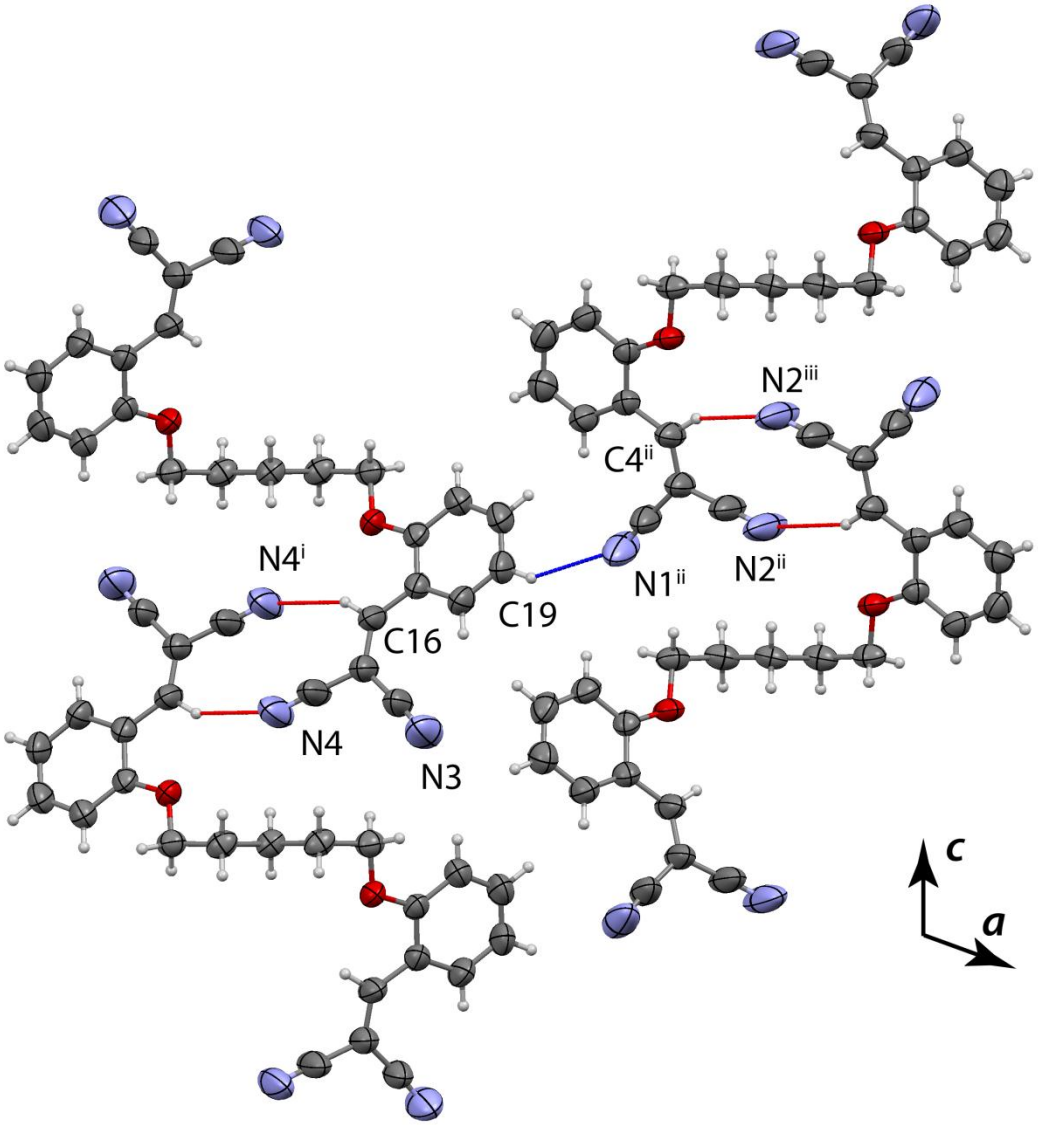

Fig. S17 Packing representation of compound **11**. Oxygen atoms indicated in red. C-H…N (red links) and C-H…N (blue links) weak hydrogen bonds connecting molecules (*i = 1-x,-1-y,1-z; ii= x, -1+y,z; iii= 1-x,-1-y,1-z*).

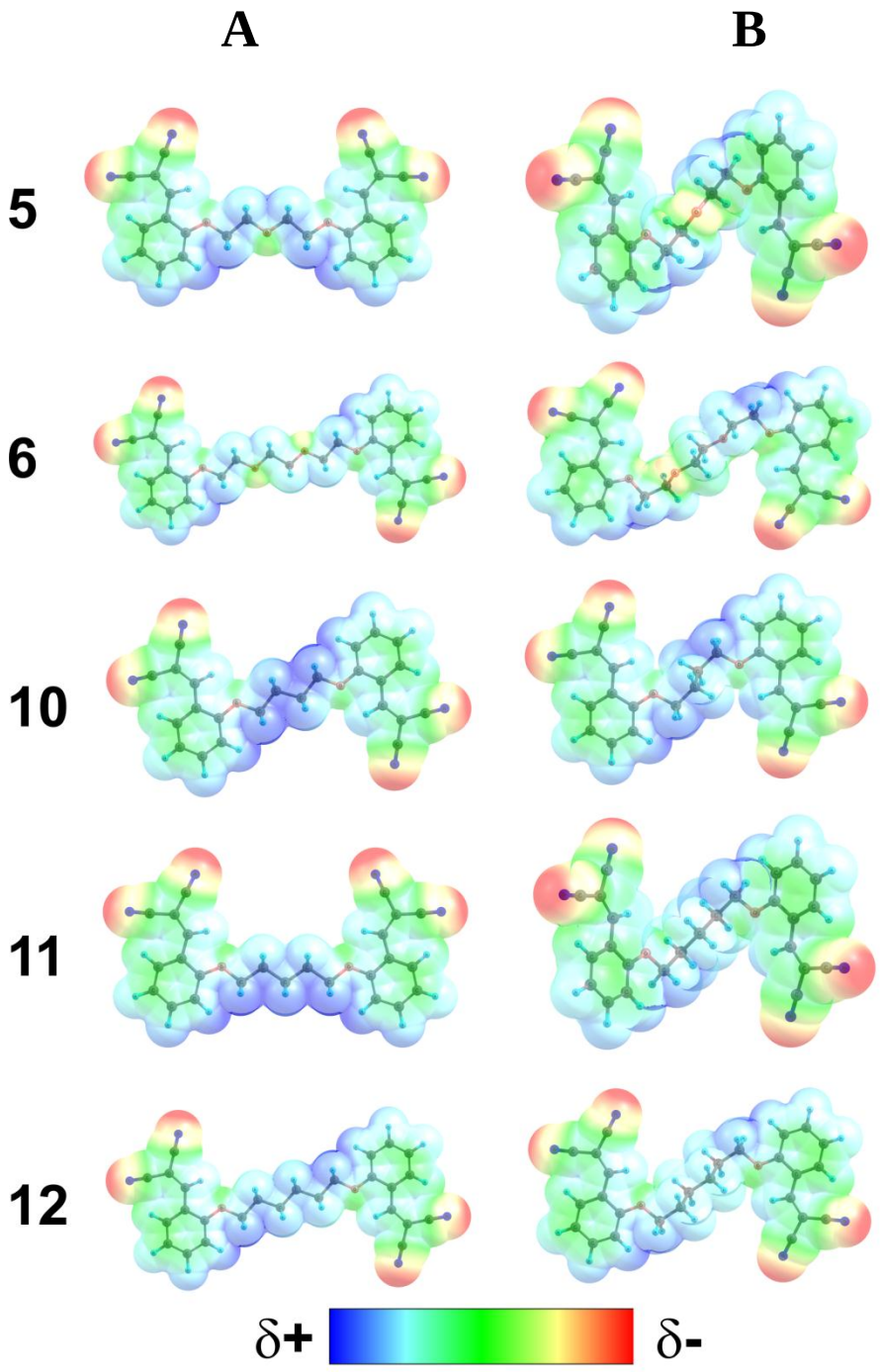

Fig. S18 Electrostatic potential surfaces for (A) the fully planar structures with zig-zag arrangement of the spacers and (B) for the structures obtained from CIF files.

Cyclic voltammetry

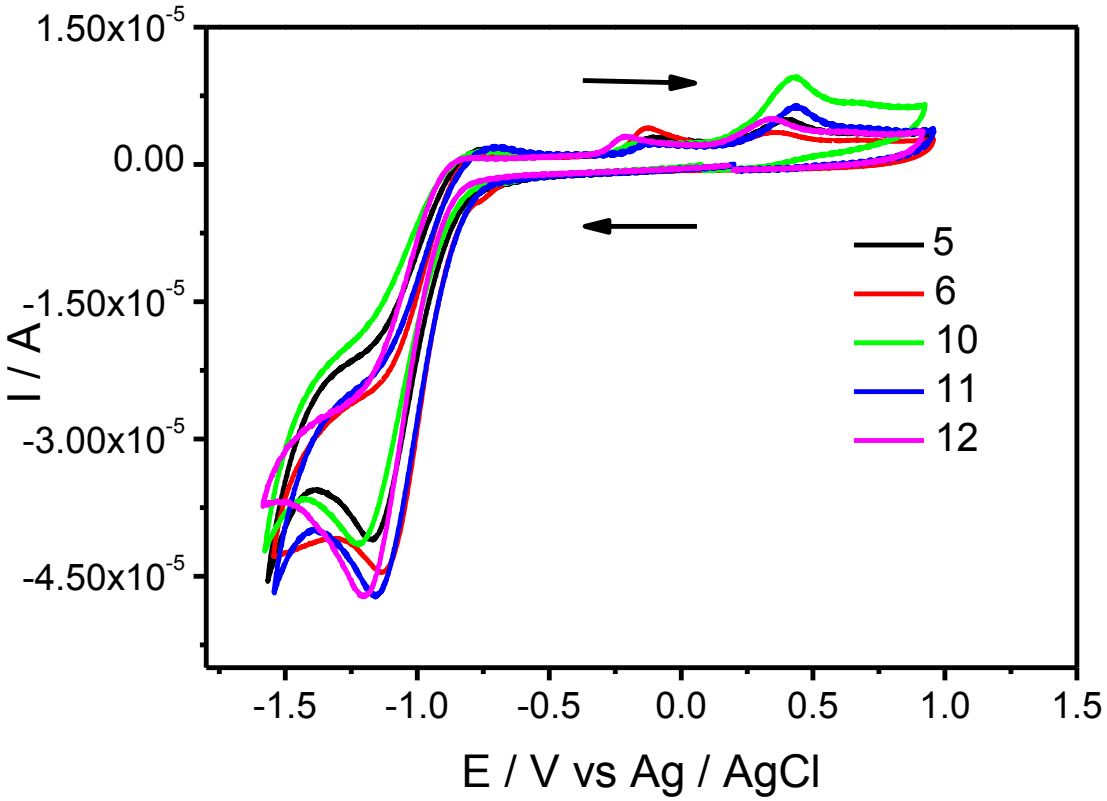

Fig. S19 The cyclic voltammograms of **5**, **6**, **10**, **11** and **12** in 0.1 mol.L^{-1} $TBAClO_4/CH_2Cl_2$ at a scan rate of 100 m.V.s^{-1}.

DFT results

Table S1 Thermodynamic properties for the equilibrium between the structures obtained from CIF files and fully planar structures with zig-zag arrangement of the spacers, calculated at B3LYP/6-31G(d,p)/PCM(CH_2Cl_2).

	5	**6**	**10**	**11**	**12**
ΔH_g^*	-2.01	-1.40	-1.26	-1.86	-0.99
ΔG_g^*	-0.77	-1.05	0.29	-0.69	0.33
ΔS_g^*	-4.17	-1.17	-5.20	-3.91	-4.45
ΔG^*_{sol}	-1.06	-1.76	0.91	0.51	1.02

Δ (Torsion [Based on X-ray structure] – Planar); (*) corresponds to the process (ideal gas, 1 mol.L^{-1}) → (ideal dilute solution, 1 mol.L^{-1}).[1,2]

Table S2 Thermodynamic properties for the equilibrium between the structures obtained from CIF files and fully planar structures with zig-zag arrangement of the spacers, calculated at B3LYP/6-31+G(d,p)/PCM(CH_2Cl_2).

	5	**6**	**10**	**11**	**12**
ΔH_g^*	-1.84	-1.21	-1.01	-1.71	-0.83
ΔG_g^*	-0.46	-1.10	-0.06	-1.47	-1.29
ΔS_g^*	-4.63	-0.39	-3.21	-0.80	1.57
ΔG^*_{sol}	-0.95	-2.04	0.60	-0.20	-0.50

Δ (Torsion [Based on X-ray structure] – Planar); (*) corresponds to the process (ideal gas, 1 mol.L^{-1}) → (ideal dilute solution, 1 mol.L^{-1}).

Table S3 Thermodynamic properties for the equilibrium between the structures obtained from CIF files and fully planar structures with zig-zag arrangement of the spacers, calculated at B3LYP/6-31+G(d,p)/PCM(CH_2Cl_2).

	5	**6**	**10**	**11**	**12**
ΔH_g^*	0.58	-9.07	-0.62	-10.41	-9.83
ΔG_g^*	2.26	-8.07	0.29	-10.87	-8.91
ΔS_g^*	-5.64	-3.36	-3.07	1.52	-3.09
ΔG^*_{sol}	-0.13	-0.57	0.57	-0.94	1.01

Δ (Torsion [Based on X-ray structure] – Planar); (*) corresponds to the process (ideal gas, 1 mol.L^{-1}) → (ideal dilute solution, 1 mol.L^{-1}).

Table S4 Thermodynamic properties for the equilibrium between the structures obtained from CIF files and fully planar structures with zig-zag arrangement of the spacers,, calculated at B3LYP/6-31+G(d,p)/(Vacuum).

	5	**6**	**10**	**11**	**12**
ΔH_g^*	0.16	1.27	-0.51	-1.08	0.11
ΔG_g^*	0.83	1.52	-0.18	-0.81	0.89
ΔS_g^*	-2.26	-0.83	-1.11	-0.91	-2.63

Δ (Torsion [Based on X-ray structure] – Planar); (*) corresponds to the process (ideal gas, 1 mol.L^{-1}) → (ideal dilute solution, 1 mol.L^{-1}).

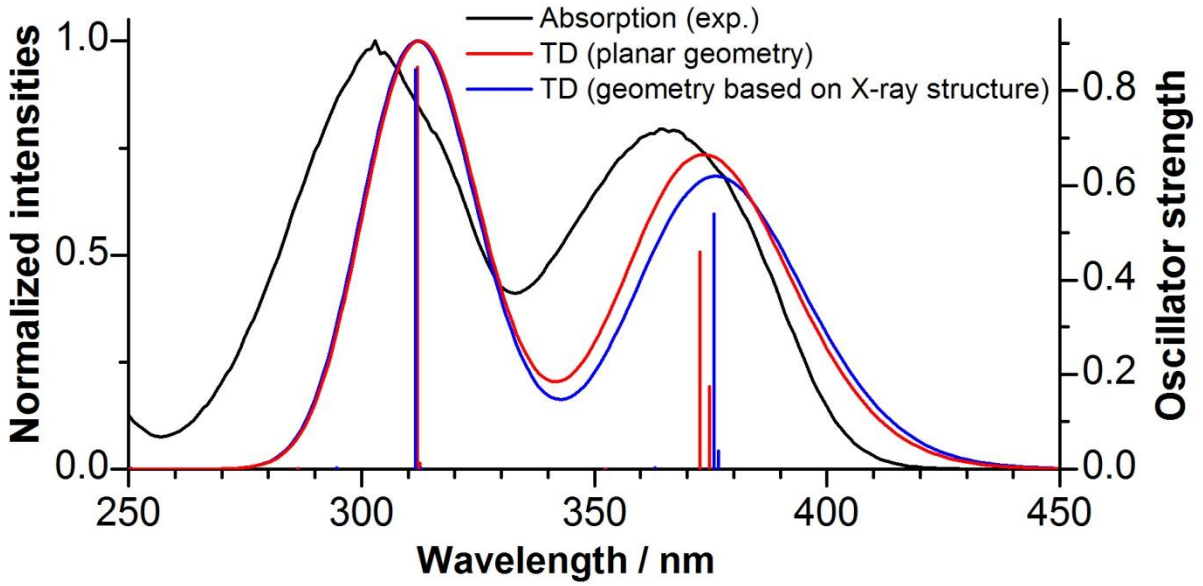

Fig. S20 Simulated electronic spectra (TD-DFT – B3LYP/6-31G(d,p)/PCM(CH_2Cl_2) of compound **5**.

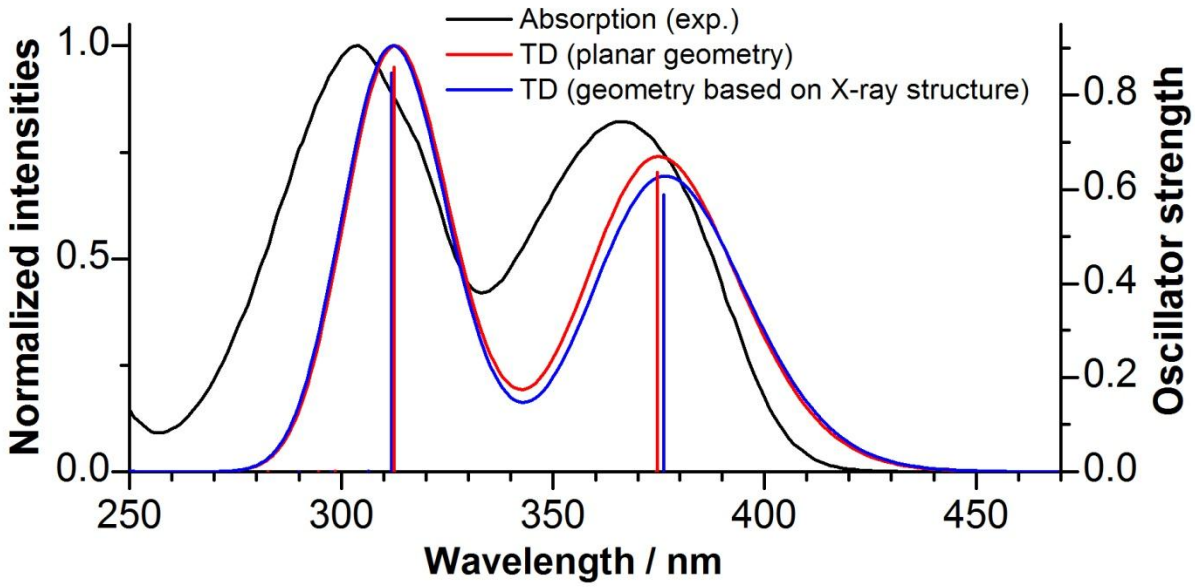

Fig. S21 Simulated electronic spectra (TD-DFT – B3LYP/6-31G(d,p)/PCM(CH_2Cl_2) of compound **6**.

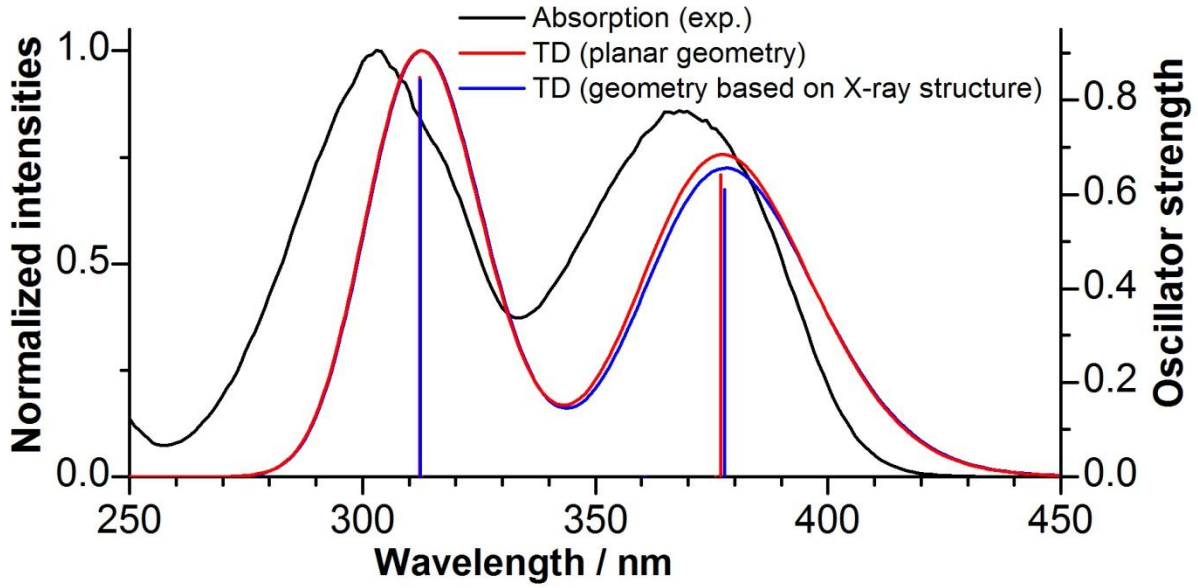

Fig. S22 Simulated electronic spectra (TD-DFT – B3LYP/6-31G(d,p)/PCM(CH_2Cl_2) of compound **10**.

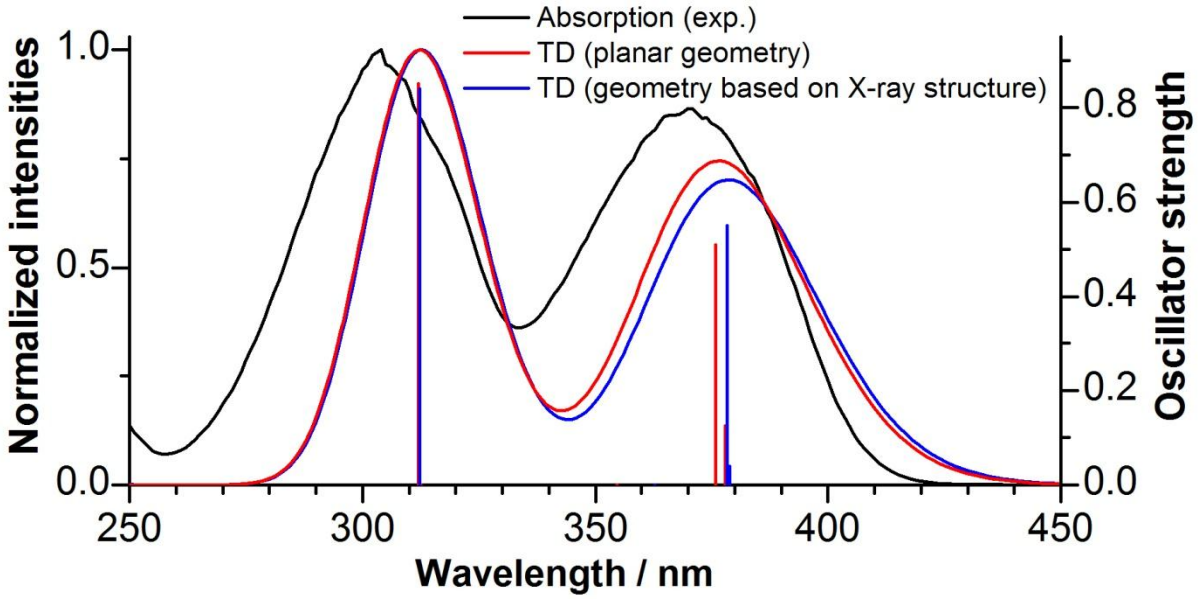

Fig. S23 Simulated electronic spectra (TD-DFT – B3LYP/6-31G(d,p)/PCM(CH_2Cl_2) of compound **11**.

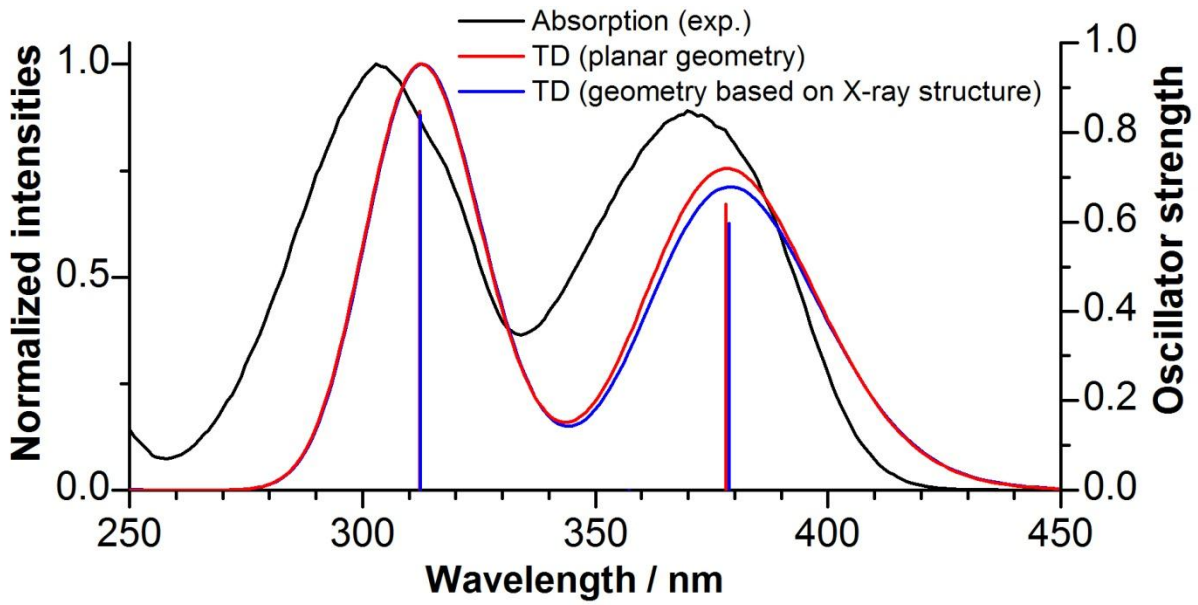

Fig. S24 Simulated electronic spectra (TD-DFT – B3LYP/6-31G(d,p)/PCM(CH_2Cl_2) of compound **12**.

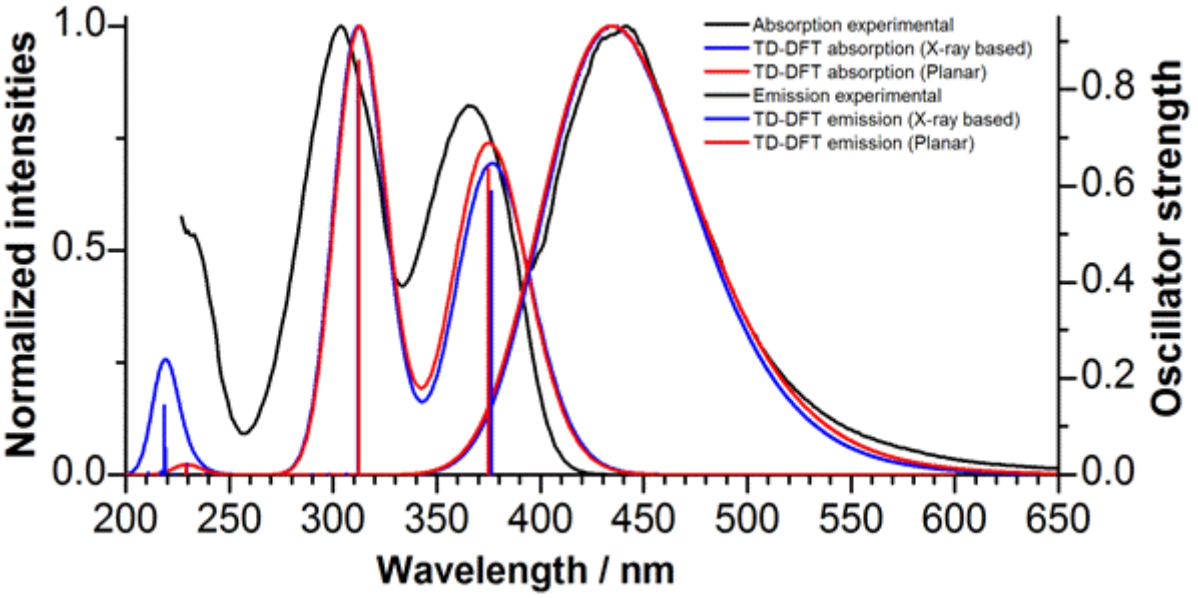

Fig. S25 Simulated absorption and emission spectra (TD-DFT – B3LYP/6-31G(d,p)/PCM(CH_2Cl_2) for the planar and X-ray geometry of compound **6** (structure obtained from CIF file).

Table S5 TD-DFT main electronic transitions calculated by B3LYP/6-31G(d,p)/PCM(CH_2Cl_2) for the structures obtained from CIF files.

Comp.	λ (exp.)	λ (TD)	*f*	contributors		Assig.
				Major	**Minor**	
5	365	376.7	0.039	H-1 → LUMO (40%) HOMO → L+1 (51%)	H-3 → LUMO (4%) H-2 → L+1 (4%)	π-π*
		375.8	0.539	H-3→ L+1 (39%) HOMO → LUMO (51%)	H-3 → L+1 (5%) H-2 → LUMO (5%)	π-π*
	303	311.5	0.844	H-3 →L+1 (42%) H-2 → LUMO (46%)	H-1 → L+1 (5%) HOMO → LUMO (5%)	π-π*
6	366	376.3	0.589	H-1→ LUMO (44%) HOMO → L+1 (45%)	H-3 → LUMO (4%) H-2 → L+1 (4%)	π-π*
	304	311.8	0.846	H-3 → LUMO (43%) H-4 → L+1 (46%)	H-1 → LUMO (5%) HOMO → L+1 (5%)	π-π*
10	369	377.8	0.611	H-1 → L+1 (43%) HOMO → LUMO (47%)	H-3 → L+1 (4%) H-2 → LUMO (5%)	π-π*
	303	312.5	0.843	H-3 → L+1 (44%) H-2 → LUMO (45%)	H-1 → L+1 (5%) HOMO → LUMO (5%)	π-π*
11	369	378.9	0.389	H-1 → LUMO (47%) HOMO → L+1 (47%)	H-3 → L+1 (4%) H-2 → LUMO (4%)	π-π*
		378.4	0.551	H-1 → L+1 (43%) HOMO → LUMO (47%)	H-3 → LUMO (7%) H-1 → L+1 (2%)	π-π*
	304	312.3	0.840	H-3 → L+1 (44%) H-2 → LUMO (45%)	H-1 → L+1 (5%) HOMO → LUMO (5%)	π-π*
12	371	378.8	0.597	H-1 → L+1 (44%) HOMO → LUMO (45%)	H-3 → L+1 (4%) H-2 → LUMO (3%)	π-π*
	303	312.4	0.838	H-3 → L+1 (44%) H-2 → LUMO (45%)	H-1 → L+1 (5%) HOMO → LUMO (4%)	π-π*

Table S6 TD-DFT main electronic transitions calculated by B3LYP/6-31G(d,p)/PCM(CH_2Cl_2) for the fully planar structures with zig-zag arrangement of the spacers.

Comp.	λ (exp.)	λ (TD)	*f*	contributors		Assig.
				Major	**Minor**	
5	365	374.8	0.1739	HOMO → LUMO (41%) H-1 → L+1 (35%)	H-3 → L+1 (4%) H-2 → LUMO (4%) H-1 → LUMO (7%) HOMO → L+1 (7%)	π-π*
		372.8	0.4595	H-1 → LUMO (36%) HOMO → L+1 (42%)	H-3 → LUMO (4%) H-2 → L+1 (4%) H-1 → L+1 (5%) HOMO → LUMO (5%)	π-π*
	303	312	0.849	H-3 → LUMO (38%) H-2 → L+1 (39%)	H-3 → L+1 (5%) H-2 → LUMO (5%) H-1 → LUMO (5%) HOMO → L+1 (5%)	π-π*
6	366	374.8	0.6358	H-1 → L+1 (44%) HOMO → LUMO (45%)	H-3 → L+1 (5%) H-2 → LUMO (5%)	π-π*
	303	312.4	0.8586	H-3 → L+1 (44%) H-2 → LUMO (44%)	H-1 → L+1 (5%) HOMO → LUMO (5%)	π-π*
10	369	377.1	0.6419	H-1 → L+1 (44%) HOMO → LUMO (46%)	H-3 → L+1 (4%) H-2 → LUMO (4%)	π-π*
	303	312.3	0.8483	H-3 → L+1 (44%) H-2 → LUMO (45%)	H-1 → L+1 (5%) HOMO → LUMO (5%)	π-π*
11	369	377.9	0.1247	H-1 → L+1 (44%) HOMO → LUMO (47%)	H-3 → L+1 (4%) H-2 → LUMO (4%)	π-π*
		375.9	0.5099	H-1 → LUMO (44%) HOMO → L+1 (46%)	H-3 → LUMO (5%) H-2 → L+1 (4%)	π-π*
	303	311.9	0.8505	H-3 → LUMO (44%) H-2 → L+1 (45%)	H-1 → LUMO (5%) HOMO → L+1 (5%)	π-π*
12	371	378.1	0.64	H-1→LUMO (45%) HOMO → L+1 (46%)	H-3 → LUMO (4%) H-2 → L+1 (4%)	π-π*
	303	312.3	0.8474	H-3 → LUMO (45%) H-2 → L+1 (45%)	H-1→ LUMO (5%) HOMO → L+1 (5%)	π-π*

Table S7. The selected bond lengths (Å) obtained for the optimized structure (from CIF file) for the ground (GS) and excited (ES) states, as well as for the first and second reduced forms of compound **6**.

Bond	GS(PCM)	ES(PCM)	GS[a](PCM)	1st red. PCM		1st red. Vacuum
				Reduced side	Neutral side	
C_9-N_{10}	1.165	1.173	1.165	1.177	1.165	1.170
$C_{9'}$-$N_{10'}$	1.164	1.171	1.165	1.175	1.165	1.169
C_8-C_9	1.430	1.414	1.430	1.410	1.430	1.423
$C_{9'}$-$C_{8'}$	1.433	1.419	1.433	1.414	1.433	1.427
C_7-C_8	**1.373**	**1.416**	**1.375**	**1.438**	**1.375**	**1.400**
C_1-C_7	1.442	1.445	1.441	1.420	1.441	1.433
C_1-C_2	**1.413**	**1.391**	**1.414**	**1.427**	**1.415**	**1.420**
C_2-C_3	**1.386**	**1.424**	**1.387**	**1.394**	**1.387**	**1.391**
C_3-C_4	1.399	1.396	1.401	1.398	1.401	1.397
C_4-C_5	1.393	1.397	1.394	1.409	1.394	1.403
C_5-C_6	1.400	1.410	1.401	1.390	1.402	1.394
C_1-C_6	**1.430**	**1.457**	**1.432**	**1.445**	**1.432**	**1.437**
C_6-O_{11}	**1.351**	**1.332**	**1.352**	**1.373**	**1.352**	**1.368**
O_{11}-C_{12}	1.435	1.447	1.439	1.426	1.439	1.423

[a]*Calculated at the B3-LYP/6-31+G (d,p)/PCM(CH_2Cl_2) level. The variation in the angles is not significant, it was not observed changes large than 2 degrees.*

Table S8. The selected bond lengths (Å) obtained from the optimized structure (using the planar geometry) for the ground (GS) and excited (ES) states, as well as for the first and second reduced forms of compound **6**.

Bond	GS(PCM)	ES(PCM)	GS[a](PCM)	1st red. PCM		1st red. Vacuum
				Reduced side	Neutral side	
C_9-N_{10}	1.165	1.173	1.165	1.176	1.165	1.170
$C_{9'}$-$N_{10'}$	1.164	1.172	1.165	1.175	1.165	1.169
C_8-C_9	1.430	1.414	1.430	1.410	1.430	1.423
$C_{9'}$-$C_{8'}$	1.433	1.419	1.433	1.414	1.433	1.427
C_7-C_8	**1.373**	**1.416**	**1.374**	**1.438**	**1.374**	**1.400**
C_1-C_7	1.442	1.444	1.442	1.420	1.442	1.433
C_1-C_2	**1.413**	**1.392**	**1.414**	**1.427**	**1.415**	**1.420**
C_2-C_3	**1.386**	**1.424**	**1.388**	**1.393**	**1.387**	**1.391**
C_3-C_4	1.399	1.396	1.401	1.398	1.401	1.397
C_4-C_5	1.393	1.396	1.394	1.409	1.394	1.403
C_5-C_6	1.399	1.409	1.400	1.389	1.400	1.393
C_1-C_6	1.431	1.457	1.432	1.444	1.432	1.436
C_6-O_{11}	**1.353**	**1.334**	**1.354**	**1.375**	**1.354**	**1.370**
O_{11}-C_{12}	1.432	1.442	1.435	1.424	1.436	1.422

[a]*Calculated at the B3-LYP/6-31+G (d,p)/PCM(CH_2Cl_2) level.*

Table S9 The computed Mulliken ($q_{Mull.}$) charges and spin densities for the different states of compound **6**, using the optimized structure obtained from CIF file.

	GS	**ES**	**GS**[a]	**1st red. PCM**			**1st red. Vacuum**	
Atom	**S_0**	**S_1**	**S_0**	**q_{Mull} Reduced side**	**q_{Mull} Neutral side**	**Spin**	**q_{Mull}**	**spin**
C_1	**0.046**	**0.108**	**0.812**	**0.628**	**0.810**	**-0.156**	**0.713**	**-0.060**
C_2	-0.123	-0.153	-0.583	-0.664	-0.588	0.293	-0.600	0.144
C_3	-0.101	-0.057	-0.402	-0.395	-0.393	-0.128	-0.370	-0.064
C_4	-0.089	-0.104	-0.782	-0.897	-0.778	0.276	-0.815	0.144
C_5	-0.134	-0.101	-0.771	0.754	0.776	-0.110	0.741	-0.052
C_6	0.346	0.341	-0.104	0.035	-0.122	0.105	-0.021	0.047
C_7	**-0.046**	**-0.142**	**0.554**	**0.297**	**0.538**	**0.554**	**0.413**	**0.247**
C_8	0.085	0.062	0.953	0.812	0.955	0.110	0.842	0.071
C_9	0.320	0.273	-0.799	-0.665	-0.793	-0.066	-0.760	-0.038
$C_{9'}$	0.298	0.264	-0.162	-0.114	-0.144	-0.028	-0.124	-0.018
N_{10}	-0.535	-0.576	-0.545	-0.698	-0.547	0.105	-0.553	0.055
$N_{10'}$	-0.516	-0.551	-0.560	-0.697	-0.560	0.074	-0.553	0.040
O_{11}	**-0.532**	**-0.451**	**-0.327**	**-0.358**	**-0.327**	**0.011**	**-0.321**	**0.005**
C_{12}	0.024	0.001	0.554	0.602	0.562	0.002	0.596	0.001

[a]*Calculated at the B3 LYP/6-31+G (d,p)/PCM(CH_2Cl_2) level.*

Table S10 The computed Mulliken ($q_{Mull.}$) charges and spin densities for the different states of compound **6** on planar geometry.

	GS	**ES**	**GS**[a]	**1st red. PCM**			**1st red. Vacuum**	
Atom	**S_0**	**S_1**	**S_0**	**Reduced side**	**Neutral side**	**Spin**		
C_1	**0.049**	**0.112**	**0.744**	**0.629**	**0.748**	**-0.159**	**0.684**	**-0.062**
C_2	-0.124	-0.155	-0.240	-0.315	-0.238	0.254	-0.264	0.123
C_3	-0.100	-0.055	-0.571	-0.550	-0.572	-0.112	-0.535	-0.056
C_4	-0.089	-0.104	-0.411	-0.510	-0.407	0.259	-0.453	0.135
C_5	-0.133	-0.101	0.092	0.121	0.091	-0.096	0.092	-0.045
C_6	0.346	0.340	0.103	0.148	0.096	0.123	0.147	0.056
C_7	**-0.045**	**-0.140**	**0.537**	**0.251**	**0.538**	**0.552**	**0.375**	**0.248**
C_8	0.086	0.064	0.832	0.668	0.827	0.116	0.720	0.074
C_9	0.323	0.278	-0.610	-0.525	-0.611	-0.053	-0.594	-0.032
$C_{9'}$	0.298	0.264	-0.251	-0.162	-0.250	-0.035	-0.212	-0.021
N_{10}	-0.535	-0.577	-0.546	-0.698	-0.548	0.106	-0.553	0.056
$N_{10'}$	-0.515	-0.549	-0.563	-0.699	-0.563	0.074	-0.555	0.040
O_{11}	**-0.542**	**-0.461**	**-0.364**	**-0.398**	**-0.364**	**0.011**	**-0.370**	**0.005**
C_{12}	0.027	0.005	0.109	0.163	0.109	0.002	0.129	0.001

[a]*Calculated at the B3 LYP/6-31+G (d,p)/PCM(CH_2Cl_2) level.*

Table S11 The computed APT charges for the different states of compound **6**, using the optimized structure obtained from CIF file.

	GS (PCM)	**GS[a](PCM)**	**1st red. PCM**		**1st red. Vacuum**
Atom	**S_0**	**S_0**	**Reduced side**	**Neutral side**	
C_1	**-0.624**	**-0.666**	**0.197**	**-0.667**	**0.556**
C_2	0.171	0.181	-0.159	0.182	-0.474
C_3	-0.417	-0.457	0.005	-0.460	0.112
C_4	0.271	0.269	-0.256	0.271	-0.647
C_5	-0.246	-0.270	0.003	-0.269	0.439
C_6	0.890	0.933	0.541	0.934	-0.277
C_7	**0.863**	**0.921**	**0.243**	**0.923**	**1.326**
C_8	-0.482	-0.532	-0.999	-0.534	-1.779
C_9	0.300	0.341	0.722	0.344	1.715
$C_{9'}$	0.432	0.501	1.032	0.499	-0.390
N_{10}	-0.461	-0.503	-0.916	-0.507	-1.470
$N_{10'}$	-0.542	-0.604	-1.078	-0.603	-0.055
O_{11}	-1.136	-1.165	-1.155	-1.165	0.291
C_{12}	0.765	0.756	0.739	0.756	0.019

[a]*Calculated at the B3 LYP/6-31+G (d,p)/PCM(CH_2Cl_2) level.*

Table S12 The computed APT charges for the different states of compound **6** on planar geometry.

	GS	**GS[a]**	**1st red. PCM**		**1st red. Vacuum**
Atom	**S_0**	**S_0**	**Reduced side**	**Neutral side**	
C_1	**-0.625**	**-0.661**	**0.203**	**-0.664**	**0.113**
C_2	0.167	0.175	-0.163	0.176	-0.454
C_3	-0.416	-0.451	0.001	-0.454	0.131
C_4	0.271	0.265	-0.259	0.267	-0.521
C_5	-0.244	-0.269	0.007	-0.268	0.266
C_6	0.890	0.928	0.533	0.930	0.011
C_7	**0.863**	**0.917**	**0.238**	**0.921**	**2.318**
C_8	-0.480	-0.522	-0.995	-0.527	-2.716
C_9	0.298	0.334	0.717	0.337	1.906
$C_{9'}$	0.429	0.496	1.030	0.498	-0.089
N_{10}	-0.460	-0.499	-0.911	-0.502	-1.651
$N_{10'}$	-0538	-0.660	-1.075	-0.600	-0.283
O_{11}	**-1.140**	**-1.164**	**-1.154**	**-1.166**	**0.417**
C_{12}	0.770	0.762	0.745	0.762	-0.178

[a]*Calculated at the B3 LYP/6-31+G (d,p)/PCM(CH_2Cl_2) level.*

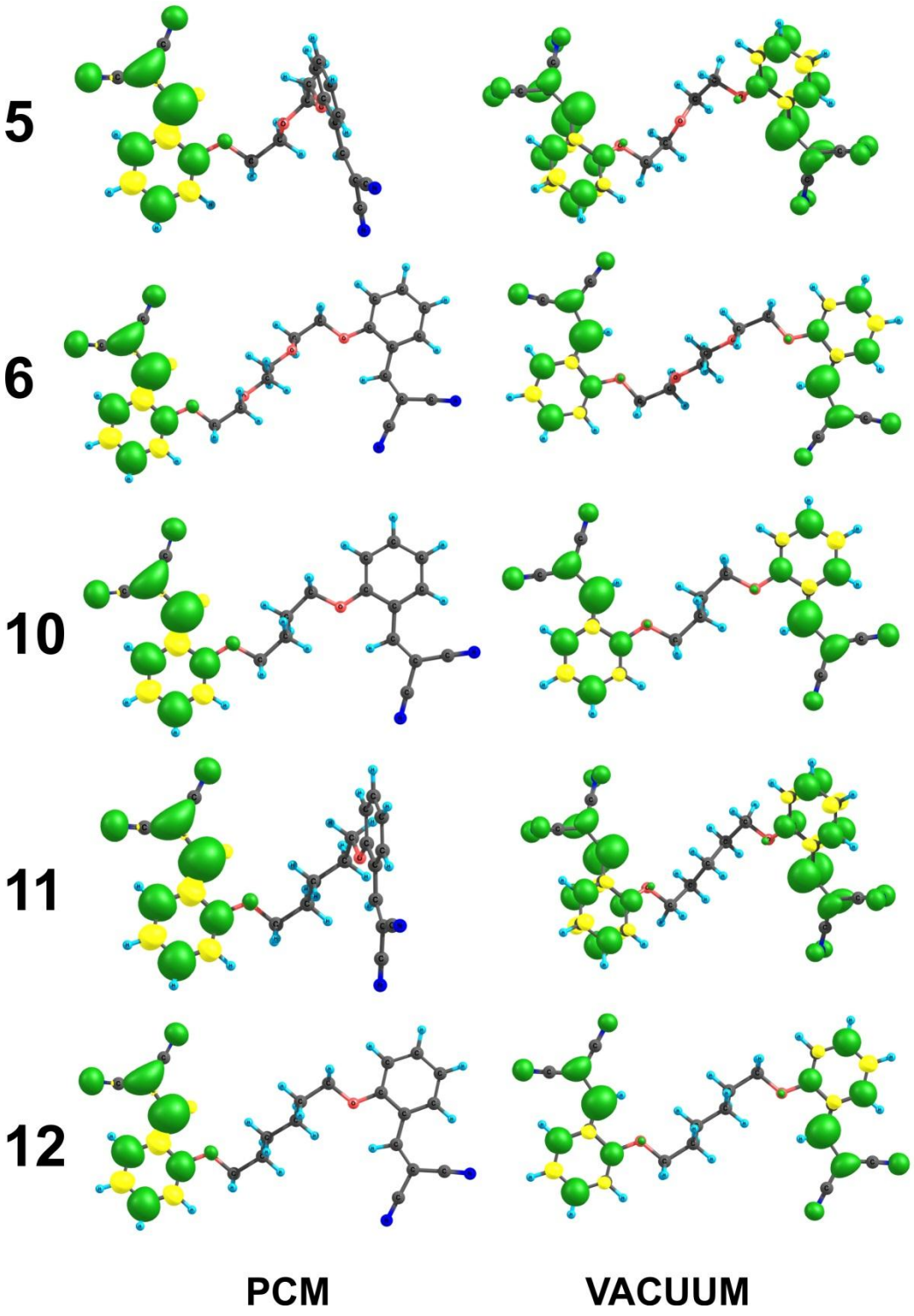

Fig. S26 The spin density distributions of the first reduction. The structures were optimized from CIF file.

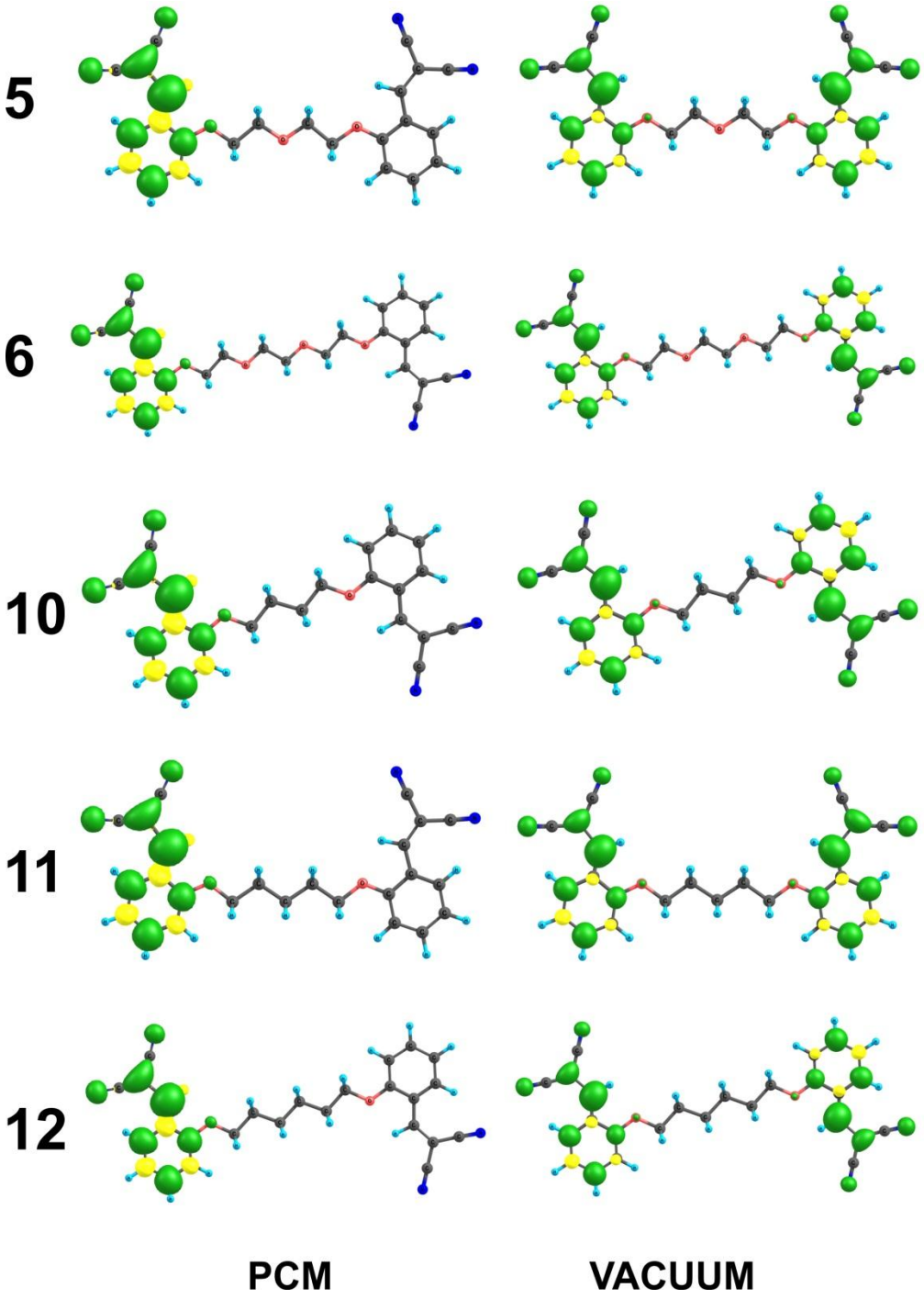

Fig. S27 The spin density distributions of the first reduction using the planar geometry.

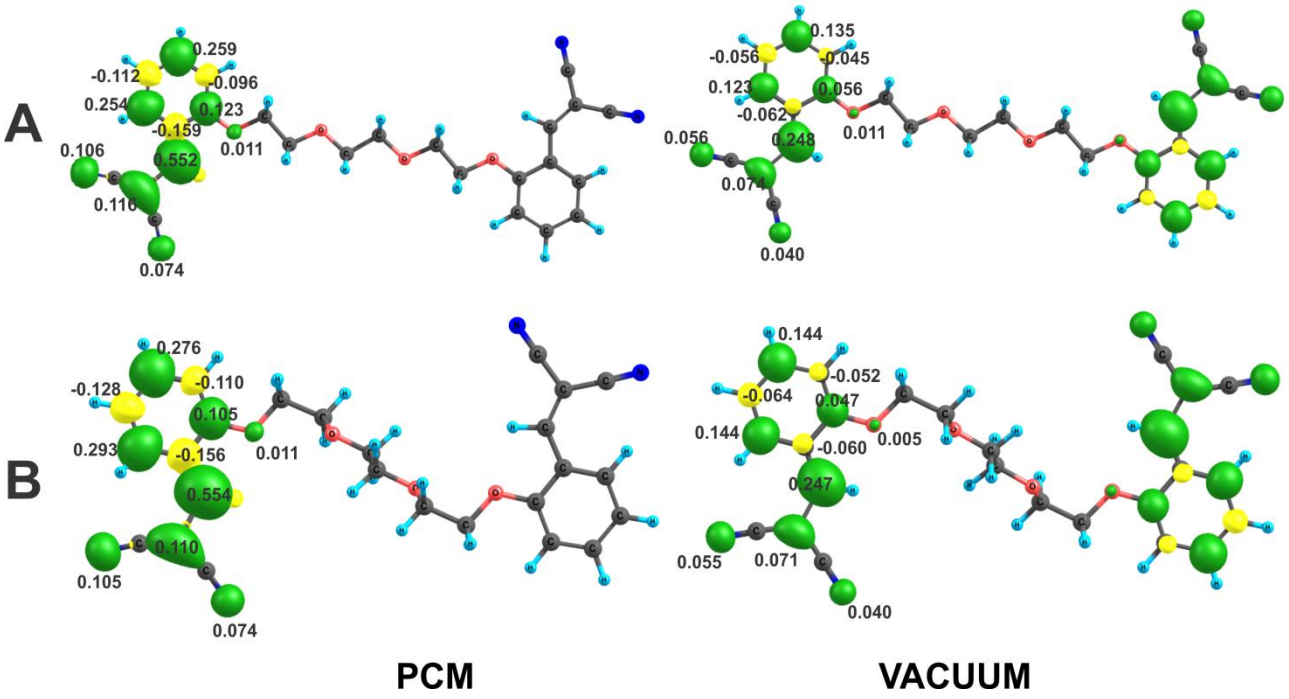

Fig. S28 The spin density distributions of the first reduction of compound **6**, forming an anion and the second reduction of compound **6**, forming a di-anion. (A) Planar geometry and (B) structure obtained from the CIF files.

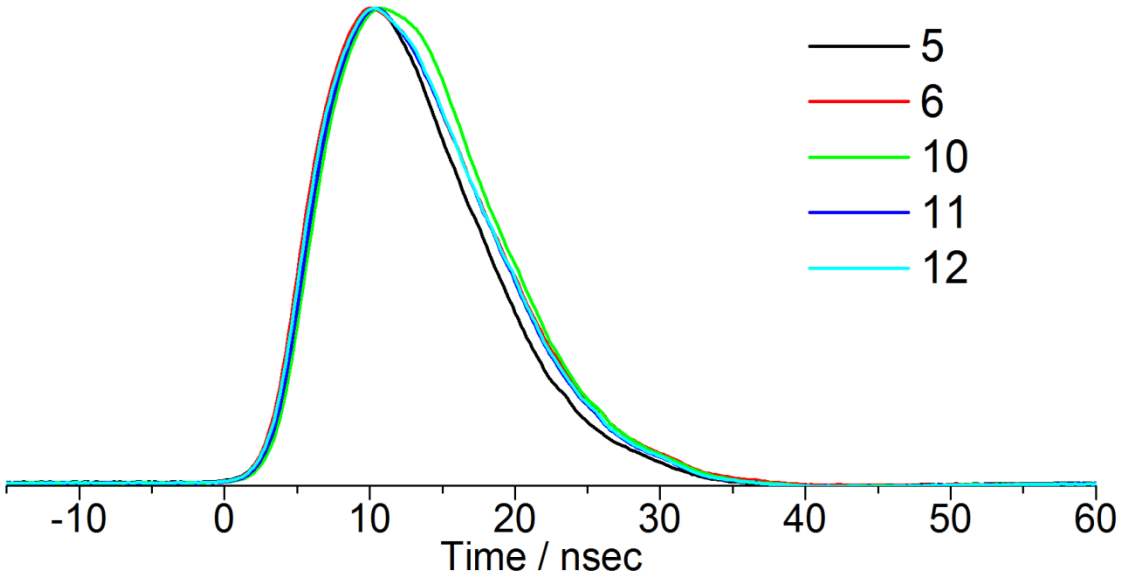

Fig. S29 Lifetime decay waveforms of the examined dicyanomethylene compounds in CH_2Cl_2.

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2 A. Ben-Naim, *J. Phys. Chem.*, 1978, **82**, 792.