Electronic Supporting Information

New Pt^{II} diimine-dithiolate complexes containing a 1,2-dithiolate-1,2-*closo*-dicarbadodecarborane: an experimental and theoretical investigation

Anna Pintus, M. Carla Aragoni, Simon J. Coles, Susanne L. Coles (née Huth), Francesco Isaia, Vito Lippolis, Ana-Daniela Musteti, Francesc Teixidor, Clara Viñas, and Massimiliano Arca*

Characterization of Compounds 2–5

Among compounds **2**–**5**, the complex **2** displayed the highest solubility in a wide range of solvents. Hence, its characterization by NMR and UV-vis spectroscopies was fully investigated. Compounds **1**, **3** and **4** showed much a lower solubility and consequently their characterization is not as complete as that described for **2**. Moreover, the very low yield of **4** did not allow for a full characterization.

[Pt(phen)(dtoc)] (2). The complex was synthesized as described for **1** starting from [PtCl$_2$(phen)] (0.21 g, 0.48 mmol). Yield: 0.12 g (42 %); m.p. > 240° C; FTIR: $\tilde{\nu}$ = 430 (vw), 453 (vw), 473 (vw), 496 (vw), 508 (w), 710 (vs), 726 (s), 763 (vw), 776 (vw), 793 (vw), 835 (vs), 867 (m), 878 (w), 929 (vw), 971 (m), 1036 (vw), 1072 (w), 1095 (w), 1110 (vw), 1147 (w), 1207 (w), 1222 (w), 1316 (vw), 1347 (vw), 1384 (vw), 1414 (w), 1429 (s), 1493 (vw), 1515 (w), 1578 (m), 1598 (w), 1629 (w), 2585 (vs), 2626 (w), 3056 (w) cm^{-1} ; UV-Vis-NIR (CH$_2$Cl$_2$): λ (ε) = 229 (30300), 271 (32700), 403 (6200), 444 nm (6200 M^{-1}·cm^{-1}); ^{1}H NMR (DMSO-d_6): δ = 8.57 (2H, dd, ^{1}J(H,H) = 8, ^{1}J(H,H) = 1), 8.41 (2H, dd, ^{1}J(H,H) = 5, ^{1}J(H,H) = 1), 7.82 (2H, s), 7.59 (2H, dd, ^{1}J(H,H) = 8, ^{1}J(H,H) = 5), ; ^{1}H{^{11}B} NMR (DMSO-d_6): δ = 8.57 (2H, dd, ^{1}J(H,H) = 8, ^{1}J(H,H) = 1), 8.41 (2H, dd, ^{1}J(H,H) = 5, ^{1}J(H,H) = 1), 7.82 (2H, s), 7.59 (2H, dd, ^{1}J(H,H) = 8, ^{1}J(H,H) = 5), 2.39 (br s,B-H), 2.18 (br s,B-H)), 1.86 (br s,B-H);^{13}C{^{1}H} NMR (DMF): δ = 147.9, 145.5, 130.8, 127.4, 126.6 (C$_{aryl}$), 85.8 (C$_{cluster}$); ^{11}B NMR (DMF): δ = –2.6 (2B, br s), –7.7 (6B, d, ^{1}J(B,H) = 139), –10.7 (2B, d, ^{1}J(B,H) = 127); elemental analysis calcd (%) for $C_{14}H_{18}N_2S_2B_{10}Pt$: C 28.91, H 3.11, N 4.81; found: C 29.31, H 3.00, N 5.00; CV (DMSO): $E_{1/2}$ *vs* Fc$^+$/Fc (scan rate = 100 mV·s^{-1}) = –1.604, –2.229 V.

[Pt(Me$_2$bipy)(dtoc)] (3). The complex was synthesized as described for **1** starting from [PtCl$_2$(Me$_2$bipy)] (0.18 g, 0.40 mmol). Yield: 0.12 g (46 %); m.p. > 240° C; FTIR: $\tilde{\nu}$ = 419 (m), 469 (vw), 492 (vw), 569 (vw), 630 (v), 639 (vw), 721 (m), 779 (vw), 824 (vs), 843 (vw), 867 (m), 927 (w), 970 (w), 1039 (w), 1074 (w), 1124 (vw), 1140 (vw), 1227 (w), 1245 (w), 1307 (w), 1382 (w), 1447 (m), 1481 (w), 1489 (w), 1551 (vw), 1619 (vs), 2575 (vs), 2624 (m), 2955 (vw), 3067 (vw) cm^{-1}; UV-Vis-NIR (CH$_2$Cl$_2$): λ (ε) = 229 (27700), 256 (sh, 14300), 288 (20000), 299 (17700), 320(sh, 6600), 347 nm (5200 $M^{-1}\cdot cm^{-1}$); $^{13}C\{^1H\}$ NMR (DMF): δ = 158.8, 146.8, 140.0, 128.6, 124.6 (C_{aryl}), 81.2 ($C_{cluster}$), 26.6 (Me); ^{11}B NMR (DMF): δ = –2.7 (2B, br s), –7.6 (6B, d, $^1J(B,H)$ = 126), –10.4 (2B, br s); elemental analysis calcd (%) for $C_{14}H_{22}N_2S_2B_{10}Pt$: C 28.61, H 4.11, N 4.76; found: C 28.98, H 3.57, N 4.80; CV (DMSO): $E_{1/2}$ *vs* Fc^+/Fc (scan rate = 100 $mV\cdot s^{-1}$) = –1.709 V.

[Pt(*t*Bu$_2$bipy)(dtoc)] (4). The complex was synthesized as described for **1** starting from [$PtCl_2$(*t*Bu$_2$bipy)] (0.15 g, 0.29 mmol). Crystals suitable for X-ray diffraction were obtained by slow infusion of petroleum ether into a dichloromethane solution of the complex. Yield: 0.10 g (50 %); m.p. > 240° C; FTIR: $\tilde{\nu}$ = 421 (w), 470 (m), 566 (vw), 597 (m), 639 (vw), 727 (m), 793 (w), 84 (s), 867 (w), 880 (m), 901 (vw), 930 (w), 973 (w), 1031 (vw), 1075 (m), 1123 (vw), 1156 (vw), 1203 (w), 1250 (m), 1307 (vw), 1369 (w), 1384 (w), 1397 (w), 1416 (m), 1448 (vw), 1467 (w), 1481 (m), 1614 (s), 2564 (vs), 2597 (vs), 2614 (vs), 2869 (vw), 2909 (vw), 2932 (vw), 2961 (s) cm^{-1}; UV-Vis-NIR (CH_2Cl_2): λ (ε) = 230 (35700), 292 (21400), 301 (22200), 438 nm (73000 $M^{-1}\cdot cm^{-1}$; ^{11}B NMR (DMF): δ = –2.7 (2B, br s), –7.6 (6B, d, $^1J(B,H)$ = 126), –10.4 (2B, br s); elemental analysis calcd (%) for $C_{20}H_{34}N_2S_2B_{10}Pt$: C 35.75, H 5.40, N 4.16; found: C 34.61, H 5.10, N 5.11; CV (DMSO): $E_{1/2}$ *vs* Fc^+/Fc (scan rate = 100 $mV\cdot s^{-1}$) = –1.698 V.

[Pt(Ph_2bipy)(dtoc)] (5). The complex was synthesized as described for 1 starting from [$PtCl_2$(Ph_2bipy)] (0.17 g, 0.30 mmol). The resulting brown precipitate was collected by filtration and recrystallized from THF. Yield: 0.04 g (4 %); m.p. > 240° C; FTIR: $\tilde{\nu}$ = 420 (m), 437 (w), 466 (m), 428 (w), 689 (m), 720 (w), 760 (s), 840 (m), 874 (w), 1103 (vs), 1384 (w), 1413 (w), 1474 (m), 1539 (w), 1597 (w), 1611 (s), 2521 (s), 2578 (s) cm^{-1}; UV-Vis-NIR (CH_2Cl_2): λ (ε) = 266 (31500), 306 (27600), 317 (26700), 458 nm (9300 $M^{-1}\cdot cm^{-1}$); $E_{1/2}$ vs Fc^+/Fc (scan rate = 100 $mV\cdot s^{-1}$) = –1.536, –2.090 V.

Table S1. Crystallographic data for complexes **1** and **4**.

	1	**4**
Empirical formula	$C_{12}H_{18}B_{10}N_2PtS_2$	$C_{20}H_{34}B_{10}N_2PtS_2$
Formula weight	557.59	669.80
Crystal size (mm)	0.42 × 0.24 × 0.04	0.34 × 0.04 × 0.02
Space group	P-1	Imma
Crystal system	Triclinic	Orthorhombic
a (Å)	6.905(10)	16.056(8)
b (Å)	12.044(3)	7.405(3)
c (Å)	12.576(3)	25.101(12)
Volume ($Å^3$)	955.31(4)	2984.4(2)
Z	2	4
Calculated density (Mg m^{-3})	1.938	1.491
Temperature (K)	120(2)	120(2)
Total number of data	4258	1900
Reflections unique	4232	1707
Parameters	246	107
R_{int}	1.3	1.0
Final *R* indices [$I > 2\sigma (I)$]	0.0376	0.0331
wR2 (all data)	0.0984	0.0653

Table S2. Selected optimized bond lengths (Å) and angles (°) for complex **1** in different solvents (IEF-PCM SCRF model).[a]

	CH_2Cl_2	$CHCl_3$	CH_3CN	Acetone	THF	DMF	Toluene
Pt–S(1)	2.302	2.300	2.305	2.304	2.302	2.305	2.295
Pt–S(2)	2.302	2.300	2.305	2.304	2.302	2.305	2.295
Pt–N(1)	2.053	2.053	2.052	2.052	2.053	2.052	2.053
Pt–N(2)	2.053	2.053	2.052	2.052	2.053	2.052	2.053
S(1)–C(1)	1.793	1.793	1.793	1.793	1.793	1.793	1.794
S(2)–C(2)	1.793	1.793	1.793	1.793	1.793	1.793	1.794
C(1)–C(2)	1.621	1.620	1.621	1.621	1.621	1.621	1.619
S(1)–Pt–S(2)	90.38	90.43	90.31	90.34	90.39	90.31	90.45
N(1)–Pt–N(2)	79.44	79.40	79.47	79.47	79.43	79.48	79.33
N(1)–Pt–S(2)–C(2)	175.43	175.22	175.38	175.44	175.41	175.37	174.14

[a] Atom labelling scheme as in Fig. 1.

Table S3. Calculated eigenvalues *E* (eV) and composition (%) of frontier KS-MOs involved in the lowest energy excitation calculated for complexes **1**–**6** in the gas phase and in DMSO (IEF-PCM SCRF model), in terms of the central Pt atom and the N^N and dtoc^{2-} ligands.

		KS-MO	*E*	N^N	dtoc^{2-}	Pt
gas	**1**	HOMO–1	–5.96	9	72	19
		LUMO	–3.23	92	3	5
	2	HOMO–1	–5.92	9	72	19
		LUMO	–3.16	92	3	5
	3	HOMO–1	–5.80	9	72	19
		LUMO	–2.99	93	3	4
	4	HOMO–1	–5.73	9	72	20
		LUMO	–2.88	93	2	4
	5	HOMO–1	–5.80	10	71	19
		LUMO	–3.12	92	3	5
	6	HOMO–1	–5.77	10	70	19
		LUMO	–3.02	92	3	5
DMSO	**1**	HOMO–1	–6.23	8	65	27
		LUMO	–2.68	95	2	4
	2	HOMO–1	–6.21	10	64	27
		LUMO	–2.64	95	1	4
	3	HOMO–1	–6.17	8	64	28
		LUMO	–2.58	95	1	3
	4	HOMO–1	–6.17	8	64	28
		LUMO	–2.49	95	1	3
	5	HOMO–1	–6.19	11	62	27
		LUMO	–2.77	94	2	4
	6	HOMO–1	–6.17	13	60	27
		LUMO	–2.70	94	2	4

Table S4. Calculated eigenvalues *E* (eV) and composition (%) of frontier KS-MOs involved in the lowest energy excitation calculated for complex **1** in different solvents (IEF-PCM SCRF model), in terms of the central Pt atom and the N^N and dtoc^{2-} ligands.

	KS-MO	*E*	N^N	dtoc^{2-}	Pt
CH_2Cl_2	HOMO–1	–6.18	8	66	26
	LUMO	–2.74	94	2	4
$CHCl_3$	HOMO–1	–6.12	8	68	25
	LUMO	–2.81	94	2	4
CH_3CN	HOMO–	–6.23	8	65	27
	LUMO	–2.68	95	2	4
Acetone	HOMO–1	–6.21	8	66	27
	LUMO	–2.70	95	2	4
DMF	HOMO–1	–6.23	8	65	27
	LUMO	–2.68	95	2	4
THF	HOMO–1	–6.16	8	67	25
	LUMO	–2.76	94	2	4
Toluene	HOMO-1	–6.05	8	69	22
	LUMO	–2.94	93	2	4

Table S5. NPA charges *Q* (e) calculated on Pt, S(1), S(2), N(1), N(2), the dtoc^{2-} ligand and the diimmine N^N for complexes **1**–**6** in the gas phase and in DMSO (IEF-PCM SCRF model).[a]

		Q(Pt)	*Q*(N1)	*Q*(N2)	*Q*(S1)	*Q*(S2)	*Q*(N^N)	*Q*(dtoc)
Gas	**1**	0.116	–0.443	–0.443	–0.002	–0.002	0.427	–0.543
	2	0.114	–0.440	–0.440	0.000	0.000	0.425	–0.540
	3	0.113	–0.448	–0.448	–0.008	–0.008	0.449	–0.562
	4	0.112	–0.446	–0.446	–0.011	–0.011	0.457	–0.570
	5	0.117	–0.447	–0.447	–0.005	–0.005	0.438	–0.555
	6	0.114	–0.443	–0.443	–0.005	–0.005	0.441	–0.555
DMSO	**1**	0.140	–0.445	–0.445	–0.056	–0.056	0.573	–0.713
	2	0.137	–0.443	–0.443	–0.052	–0.052	0.570	–0.707
	3	0.134	–0.452	–0.452	–0.059	–0.059	0.591	–0.725
	4	0.134	–0.500	–0.500	–0.060	–0.060	0.594	–0.727
	5	0.139	–0.449	–0.449	–0.056	–0.056	0.577	–0.717
	6	0.137	–0.445	–0.445	–0.054	–0.054	0.575	–0.712

[a] Atom labelling scheme as in Fig. 1.

Table S6. NPA charges *Q* (e) calculated on Pt, S(1), S(2), N(1), N(2), the dtoc^{2-} ligand and the diimmine N^N for **1** in different solvents (IEF-PCM SCRF model).[a]

	Q(Pt)	*Q*(N1)	*Q*(N2)	*Q*(S1)	*Q*(S2)	*Q*(N^N)	*Q*(dtoc)
CH_2Cl_2	0.137	–0.445	–0.445	–0.049	–0.049	0.555	–0.692
$CHCl_3$	0.134	–0.444	–0.444	–0.042	–0.042	0.536	–0.670
CH_3CN	0.140	–0.455	–0.455	–0.055	–0.055	0.572	–0.712
Acetone	0.139	–0.445	–0.445	–0.054	–0.054	0.568	–0.707
DMF	0.140	–0.445	–0.445	–0.056	–0.056	0.572	–0.712
THF	0.136	–0.445	–0.445	–0.047	–0.047	0.550	–0.687
Toluene	0.128	–0.444	–0.444	–0.029	–0.029	0.501	–0.629

[a] Atom labelling scheme as in Fig. 1.

Table S7. Main electronic singlet transitions (*f* > 0.005) calculated for **2** in DMSO (IEF-PCM SCRF model) at the TD-DFT level. For each transition, the excitation energy *E* (eV), the absorption wavelength λ (nm), the oscillator strength *f*, and the molecular orbital composition (%) of the excited-state functions, along with the fragments where the involved KS-MOs are mainly localized, are reported.

Exc. state	*E* (eV)	λ(nm)	*f*	Composition[a]	%	Assignment
S2	2.771	447.4	0.066	107→109	73	dtoc^{2-}(64%)+Pt(27%)→phen(95%)
S3	2.993	414.2	0.144	108→110	73	dtoc^{2-}(73%)+Pt(24%)→phen(99%)
S4	3.054	406.0	0.029	107→110	97	dtoc^{2-}(64%)+Pt(27%)→phen(99%)
S5	3.162	392.1	0.010	108→111	92	dtoc^{2-}(73%)+Pt(24%)→dtoc^{2-}(46%)+Pt(37%)
S12	4.280	289.6	0.040	107→112	87	dtoc^{2-}(64%)+Pt(27%)→phen(98%)
S14	4.504	275.3	0.097	104→109	35	phen(78%)→phen(95%)
				102→109	27	dtoc^{2-}(53%)+phen(28%)→phen(95%)
				100→109	14	dtoc^{2-}(37%)+Pt(37%)→phen(95%)
S15	4.519	274.3	0.023	103→109	92	dtoc^{2-}(45%)+Pt(44%)→phen(95%)

[a] The MOs are labelled according to Fig. S3.

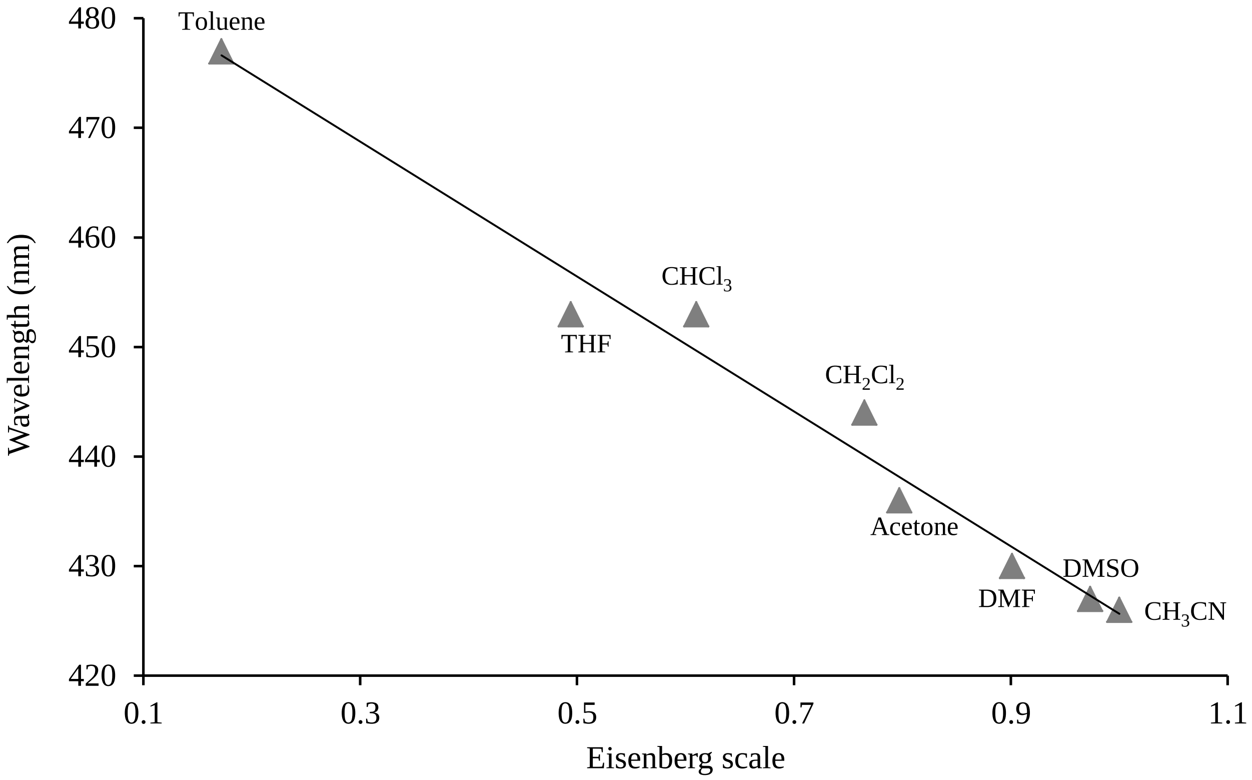

Fig. S1. Correlation between the lowest energy absorption maxima λ_{max} in the visible region in eight solvents for complex **2** and the empirical scale formulated by Eisenberg for [Pt(N^N)(S^S)] complexes (R^2 = 0.98; Table 2).

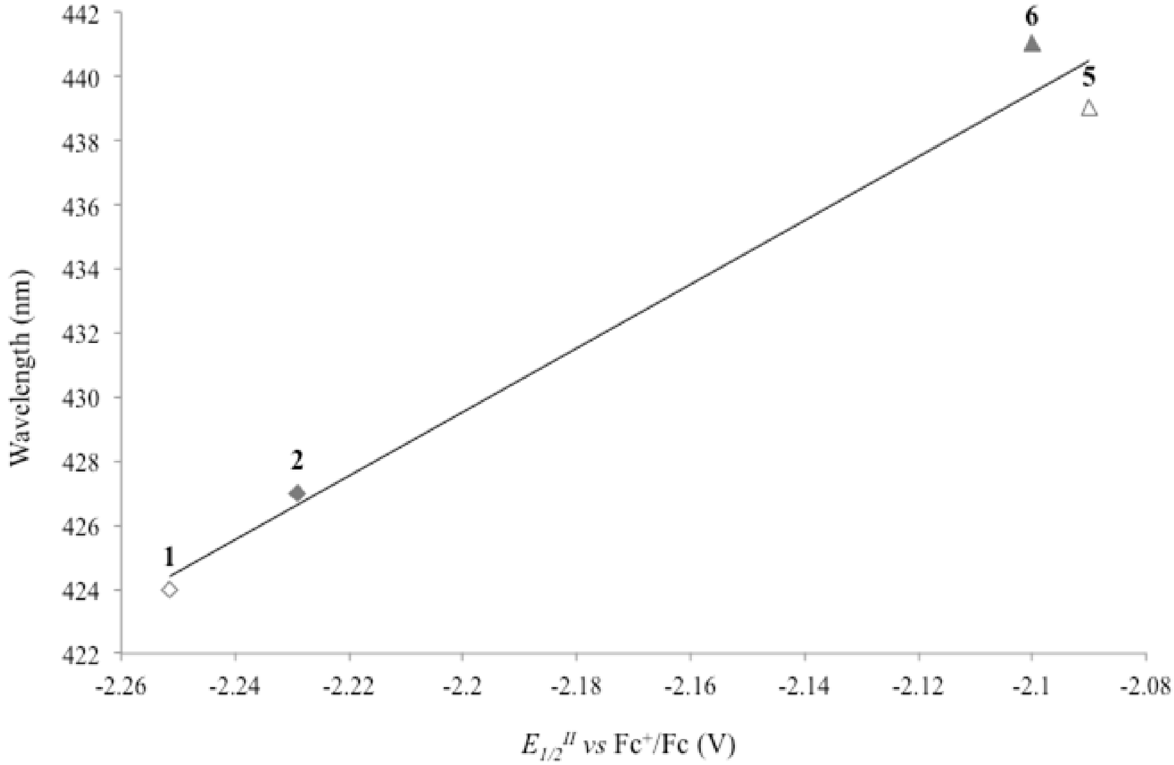

Fig. S2. Correlation between the reduction potentials $E_{1/2}{}^{II}$ (V *vs* Fc$^+$/Fc) and the λ_{max} of the solvatochromic absorption (nm) in DMSO solutions of complexes **1**–**2** and **5**–**6** (R^2 = 0.98; Tables 2 and 3). N^N = unsubstituted (rhombs) 2,2'-bipyridine (empty) or 1,10-phenathroline (filled), and alkyl (circles) or phenyl (triangles) derivatives.

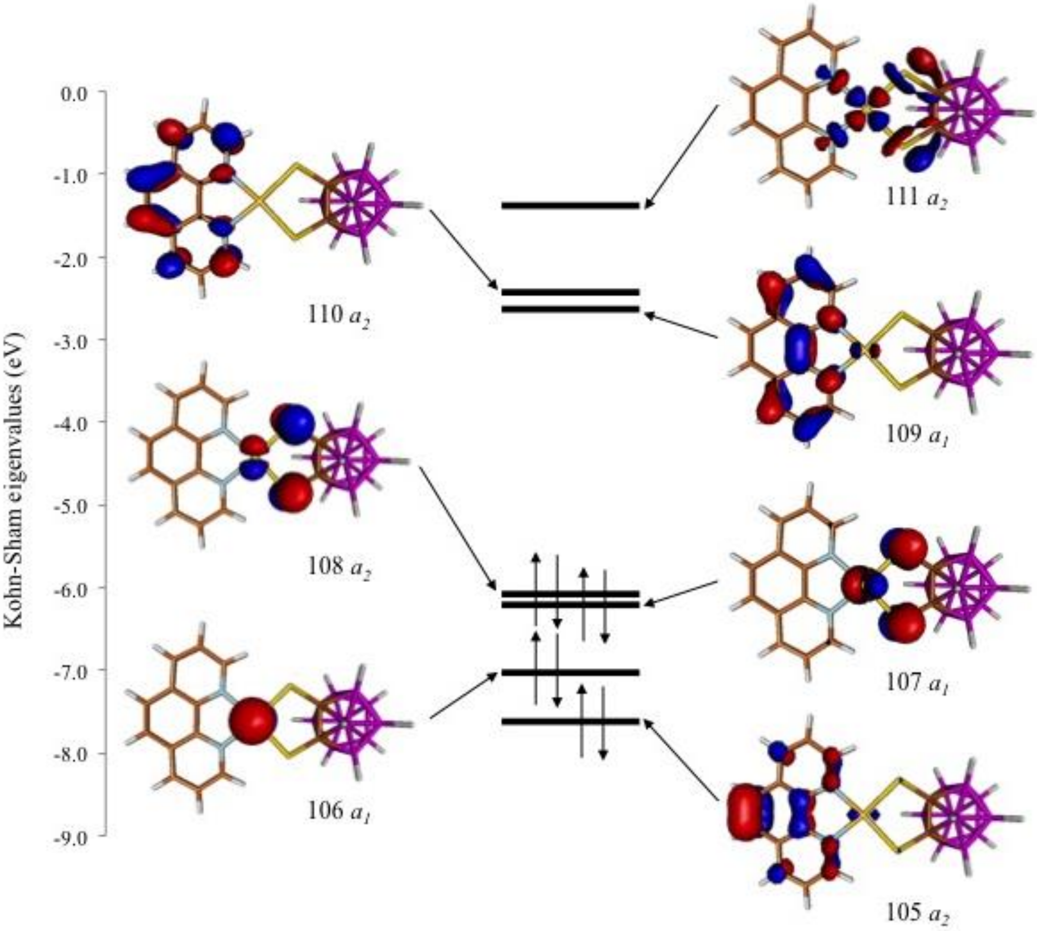

Fig. S3. KS-MO scheme and isosurface drawings calculated for **2** in DMSO (IEF-PCM SCRF model; C_s point group; contour value = 0.05 e).

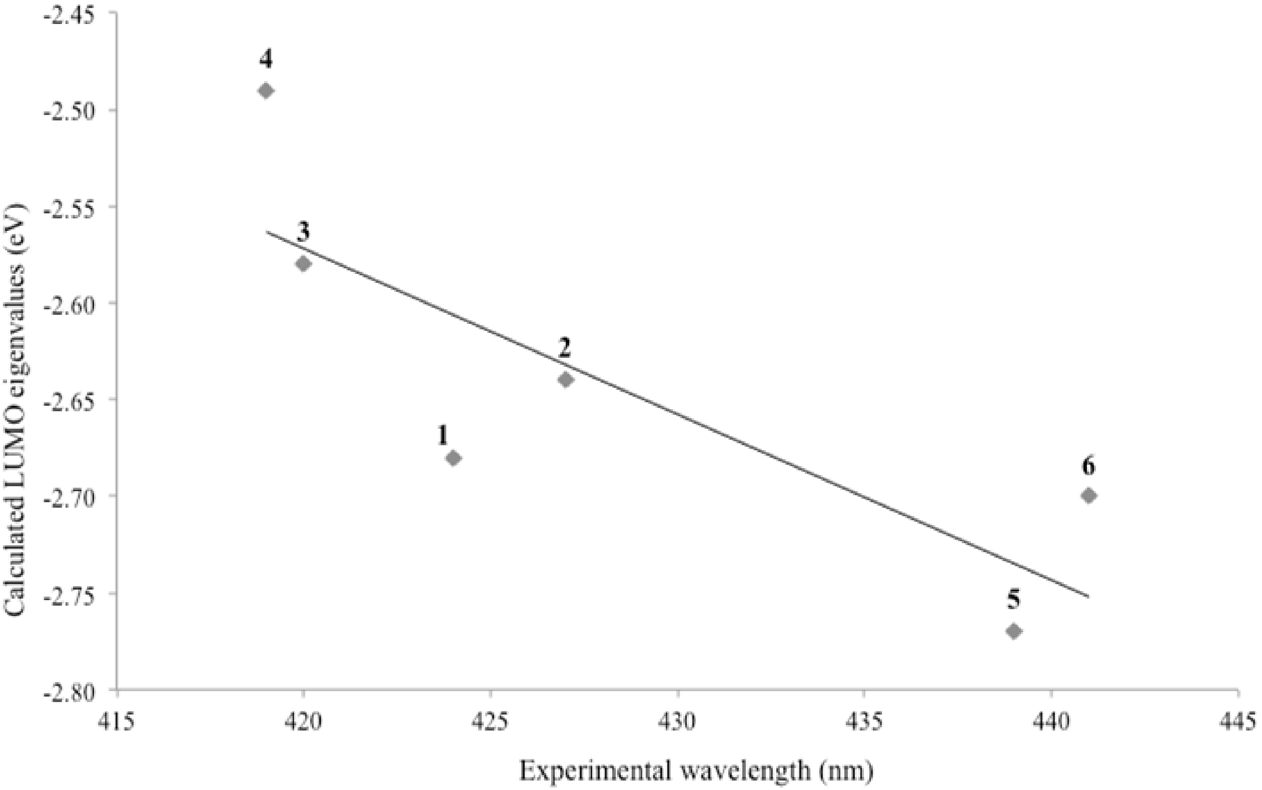

Fig. S4. Correlation between the experimental λ_{max} (nm) of lowest energy solvatochromic absorption in the Vis region and the IEF-PCM TD-DFT calculated LUMO energy (eV) for complexes **1**–**6** in DMSO (R^2 = 0.69; Tables 2 and S3). N^N = unsubstituted (rhombs) 2,2'-bipyridine (empty) or 1,10-phenathroline (filled), and alkyl (circles) or phenyl (triangles) derivatives.

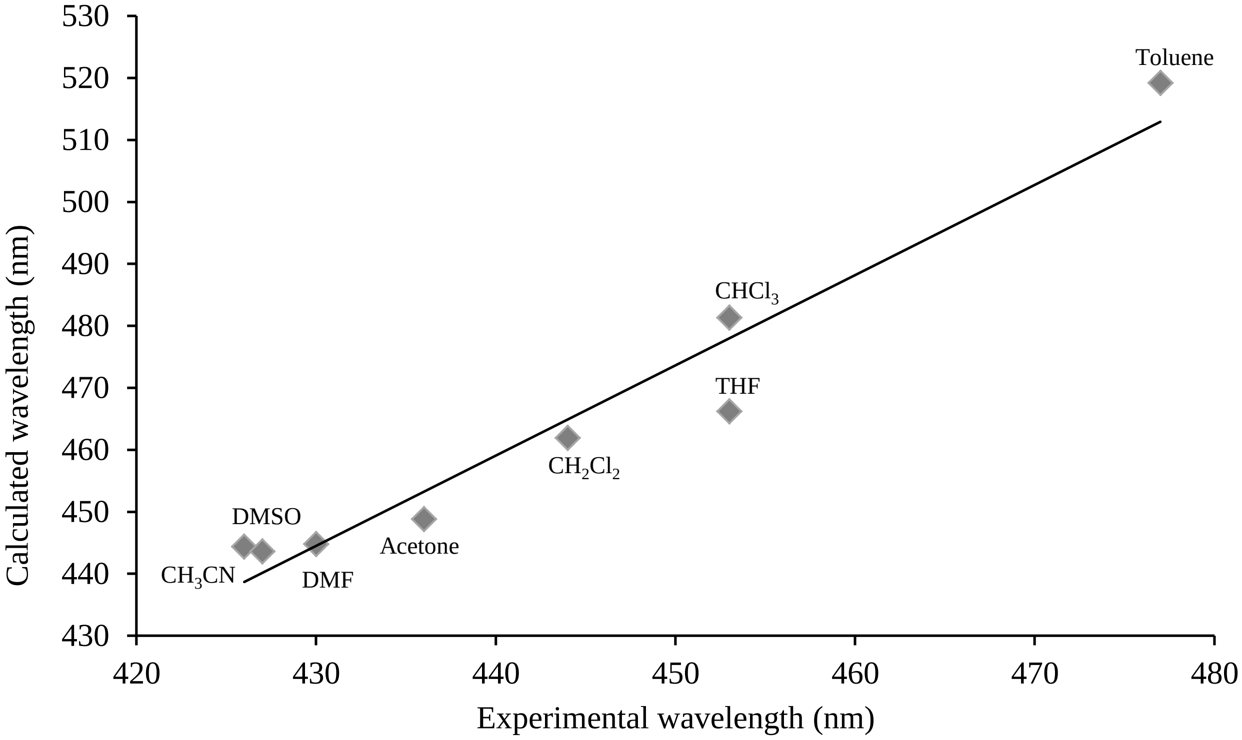

Fig. S5. Experimental and IEF-PCM SCRF TD-DFT calculated λ_{max} (nm) of the lowest energy solvatochromic absorption band in the visible region for **1** in different solvents (R^2 = 0.94; Table 2).