

Supplementary information to accompany

Rich Redox-Activity and Solvatochromism in a Family of Heteroleptic Cobalt Complexes

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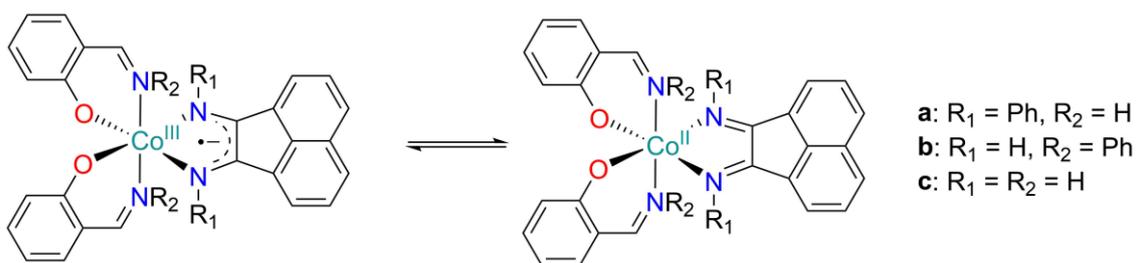


Chart S1 Valence tautomeric equilibria of complexes computationally predicted to exhibit VT.¹

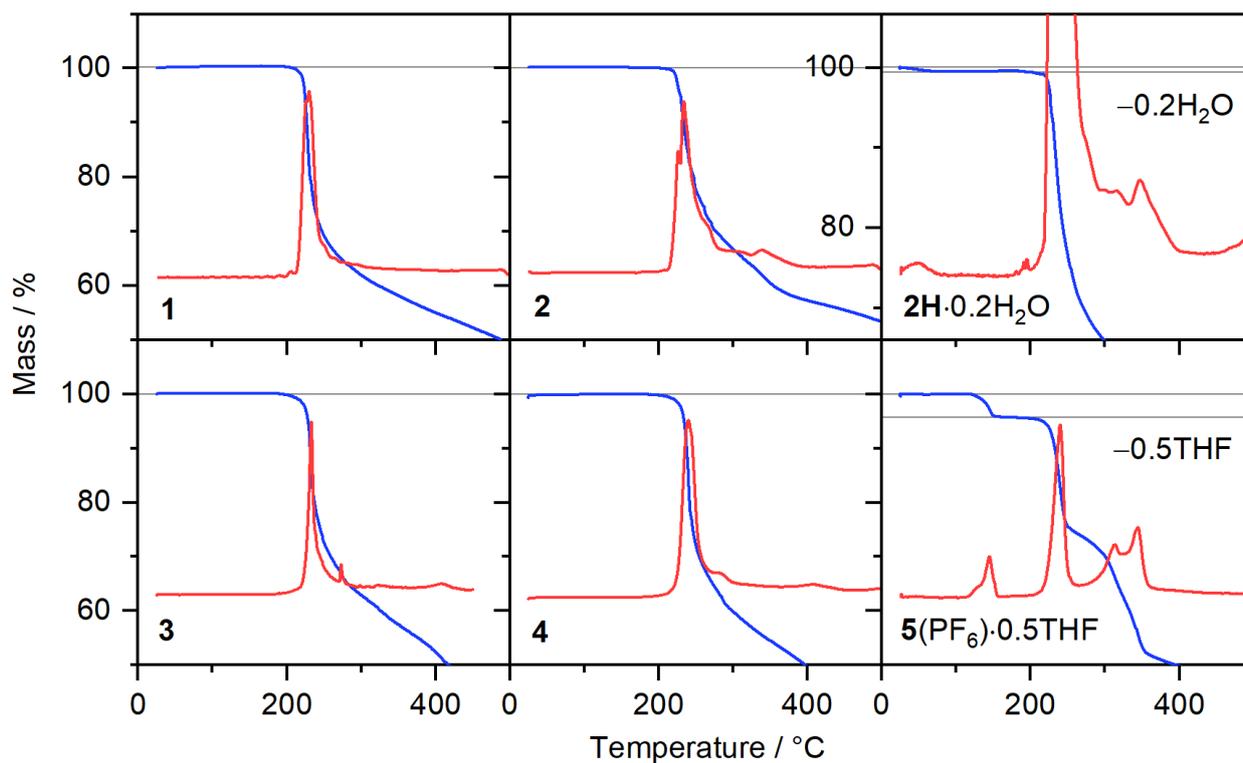


Fig. S1 Thermogravimetric analysis of **1**, **2**, **2H·0.2H₂O**, **3**, **4**, and **5(PF₆)·0.5THF**. Mass loss profile in blue, and scaled negative of the first derivative in red.

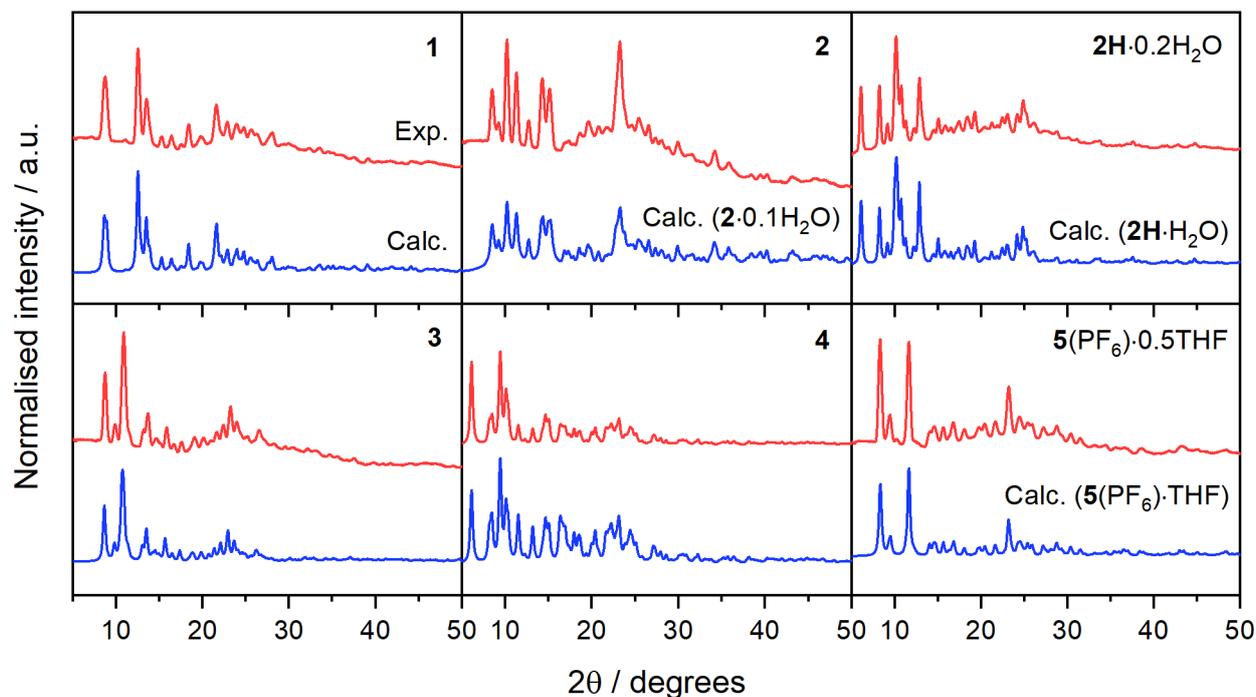


Fig. S2 Calculated PXRD patterns of the crystal structures (blue) vs. experimental PXRD patterns of the bulk samples of **1**, **2**, **2H**·0.2H₂O, **3**, **4**, and **5(PF₆)**·0.5THF (red). All measurements collected at 100 K, except for **3** (300 K) and **5(PF₆)**·0.5THF (175 K). For **2**, the theoretical pattern is calculated from the crystal structure of the freshly mounted crystal, **2**·0.1H₂O. The agreement of the experimental pattern of **2** with the calculated pattern of **2**·0.1H₂O indicates that the partial loss of solvent in the bulk sample is not accompanied by a loss in crystallinity. Likewise, for **2H**·0.2H₂O, the theoretical pattern is calculated from the crystal structure of the freshly mounted crystal, **2H**·H₂O. The agreement of the experimental pattern of **2**·0.2H₂O with the calculated pattern of **2**·H₂O indicates that the partial loss of solvent in the bulk sample is not accompanied by a loss in crystallinity. Finally, for **5(PF₆)**·0.5THF, the theoretical pattern is calculated from the crystal structure of the freshly mounted crystal, **5(PF₆)**·THF, with the agreement of the patterns again indicating that the bulk and crystal are of the same phase.

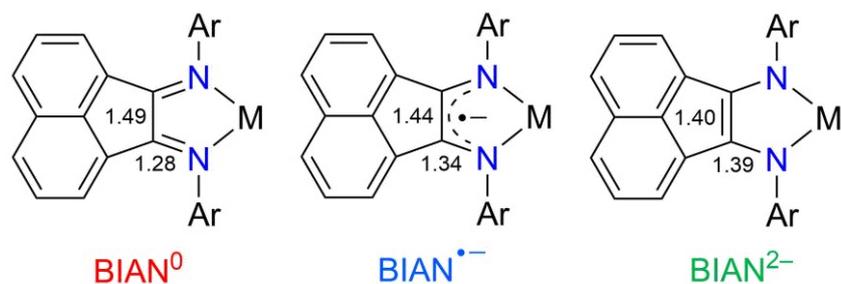


Fig. S3 Neutral, monoanionic radical, and dianionic oxidation states of coordinated BIAN, with typical bond lengths of the C₁–C₂ and imine C–N bonds displayed.^{2–4}

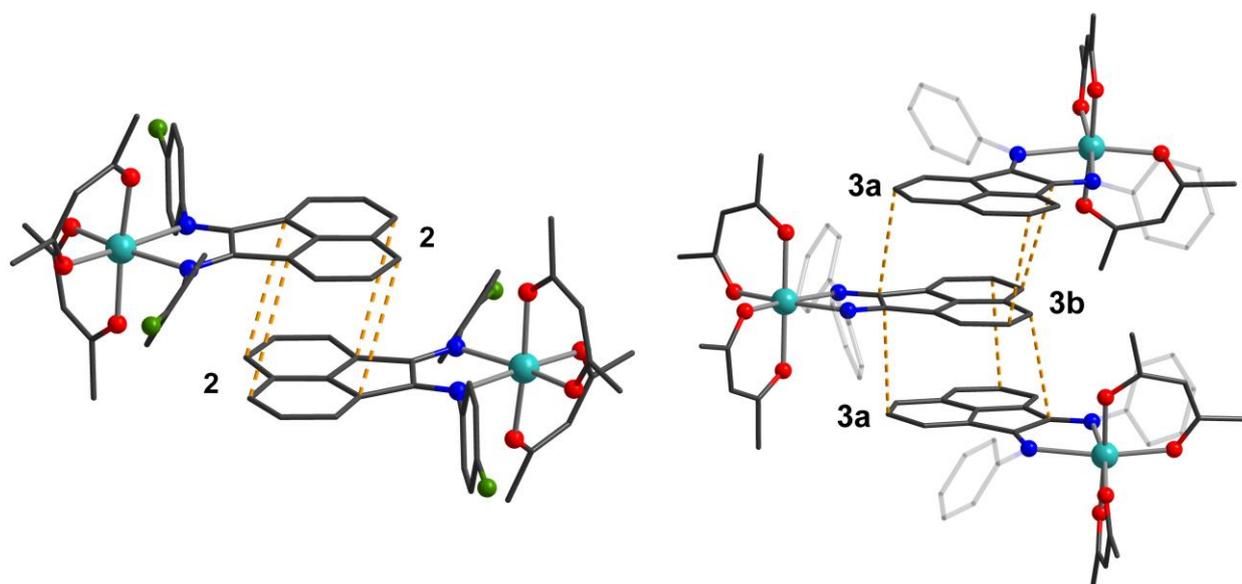


Fig. S4 π - π stacking interactions between acenaphthene moieties of molecules of **2** in **2**·0.1H₂O (left) and **3a** and **3b** in **3** (right). Hydrogen atoms omitted for clarity. Colour code: C (grey), N (blue), O (red), Co (aqua), Cl (dark green).

Table S1 Plane-plane distance, d , between pairs of acenaphthene moieties in the structures of **1**, **2**·0.1H₂O, **4** and **5**(PF₆)·THF. Since d is undefined in the structure of **3**, an average point-plane distance is listed instead.

1	2 ·0.1H ₂ O	3	4	5 (PF ₆)·THF
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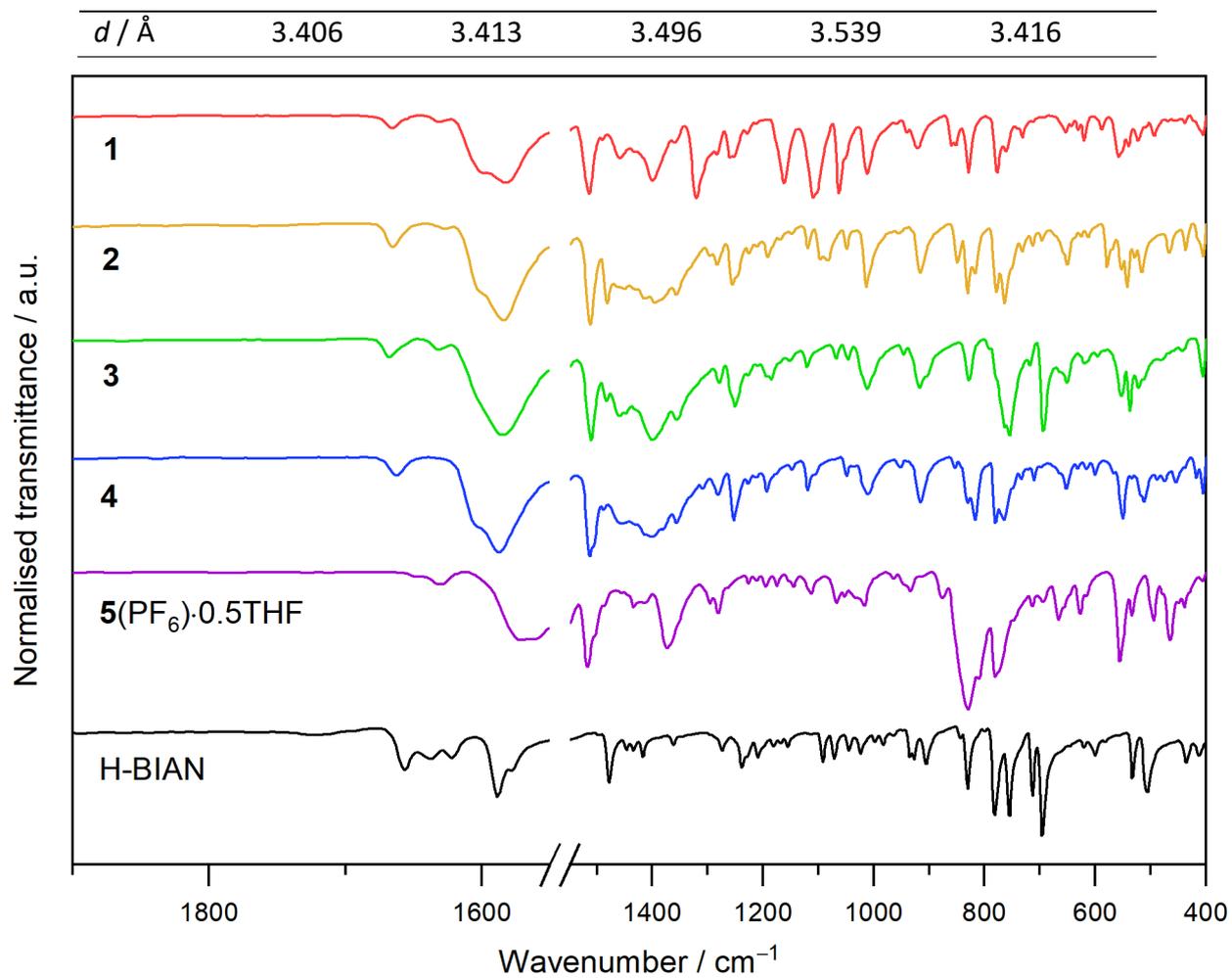


Fig. S5 ATR-IR spectra of H-BIAN, **1–4**, and **5(PF₆)·0.5THF**. The region above 1550 cm^{-1} is at an increased scale to highlight the characteristic C=N signals in this vicinity.

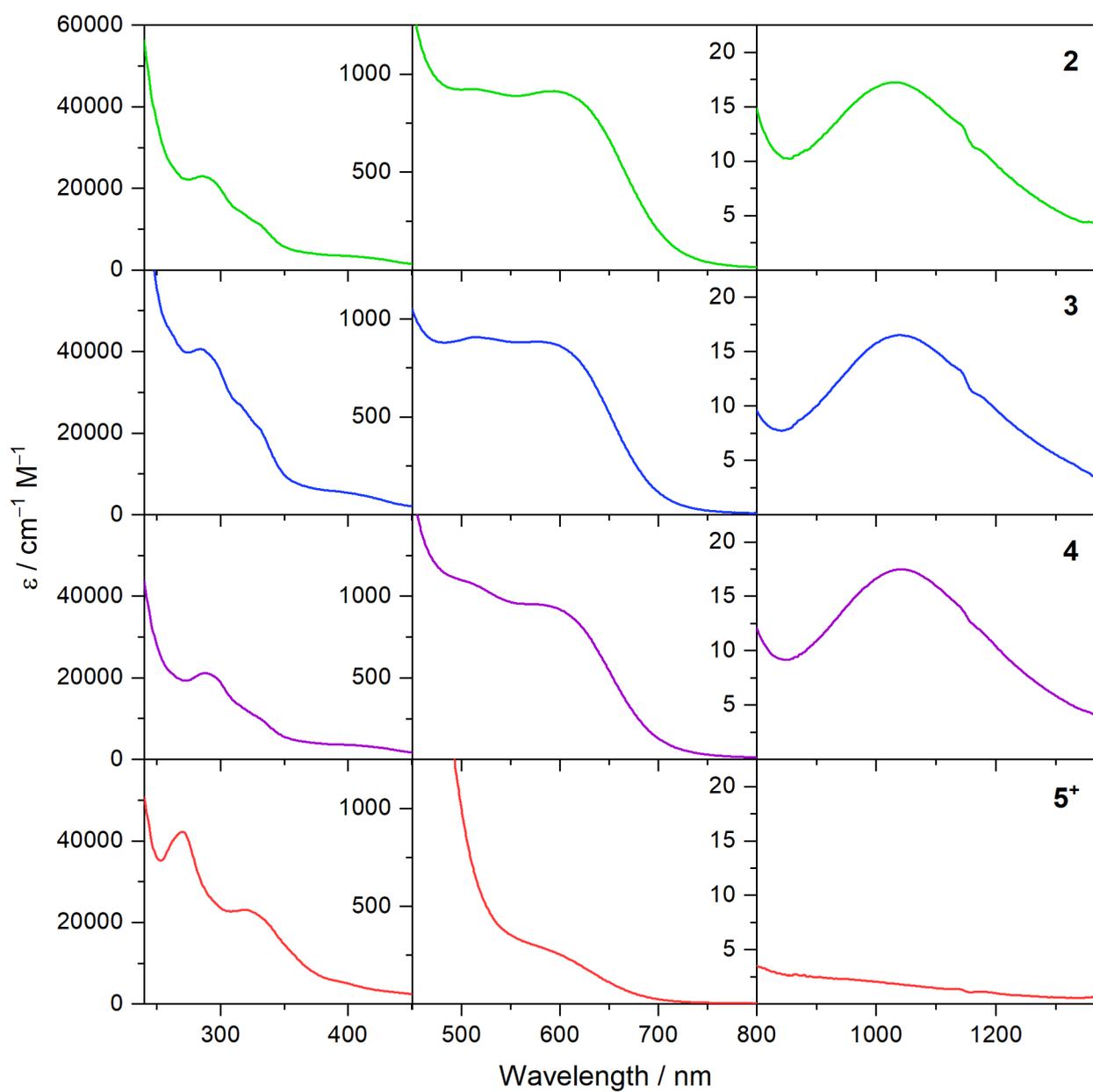


Fig. S6 UV-vis-NIR absorbance spectra of **2–4** and **5⁺** in DCM. Equivalent plot for **1** presented in main text (Fig. 3).

Table S2 Peak maximum of ${}^4T_1(F) \rightarrow {}^4T_2$ transition of **1–4** in DCM solution.

	1	2	3	4
$\lambda_{\max} / \text{nm}$	1022	1032	1040	1042

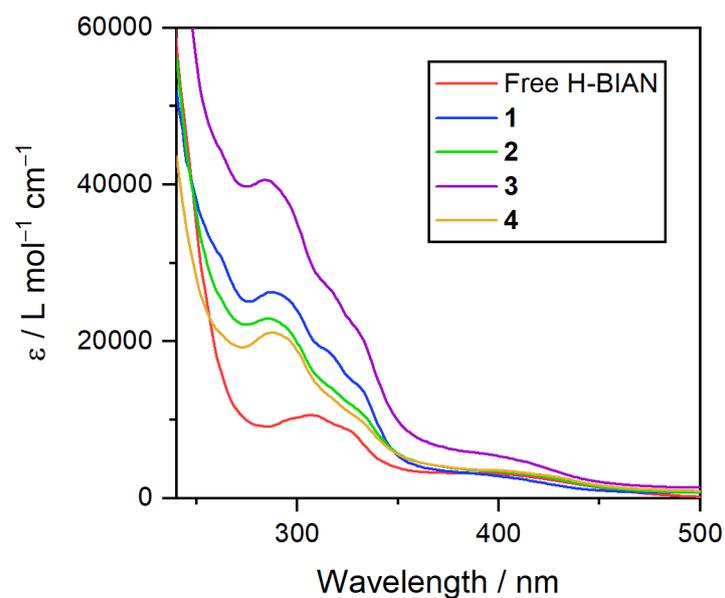


Fig. S7 UV-vis absorbance spectra of **1–4** in DCM compared with that of free H-BIAN.

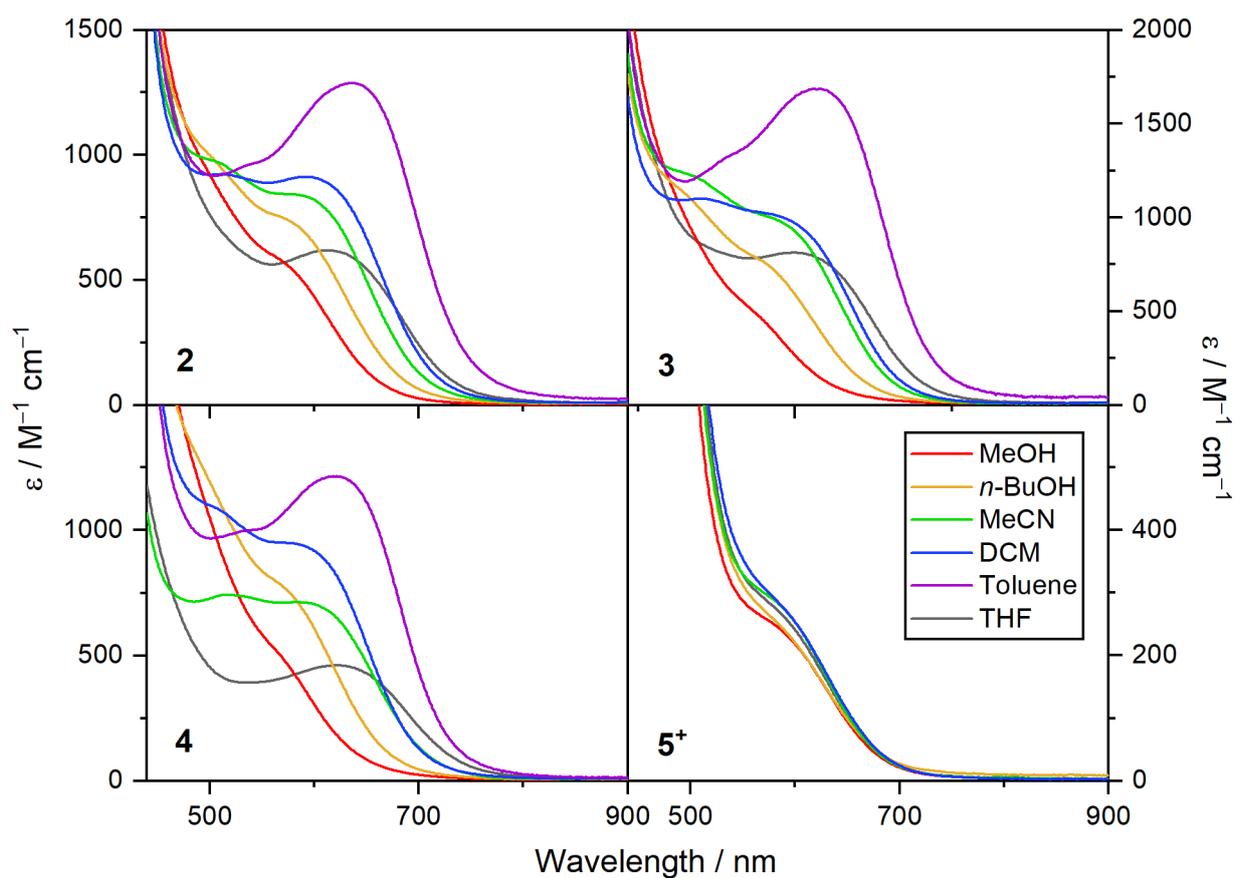


Fig. S8 Visible region spectra of **2**, **3**, **4**, and **5⁺** in various solvents. Equivalent plot for **1** presented in main text (Fig. 5).

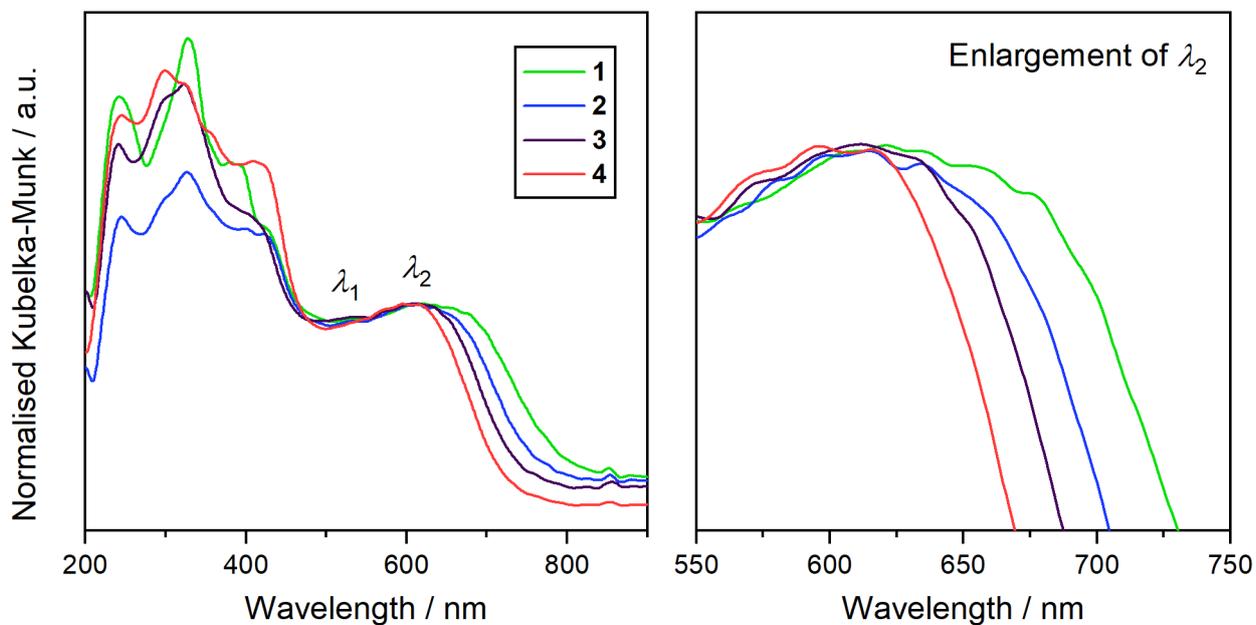


Fig. S9 Diffuse reflectance spectra ($\sim 1\%$ in KBr) of **1–4**, normalised to the λ_2 transition. Right: diffuse reflectance spectra enlarged on the λ_2 transition.

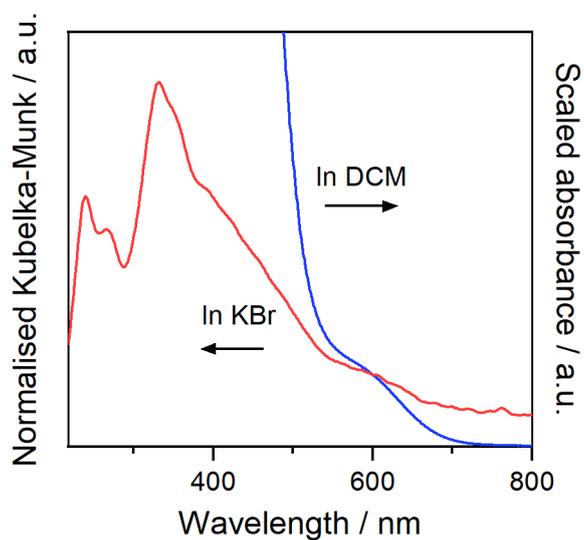


Fig. S10 Comparison of the diffuse reflectance spectrum of **5(PF₆)·0.5THF** ($\sim 1\%$ in KBr) with the solution state spectrum in DCM.

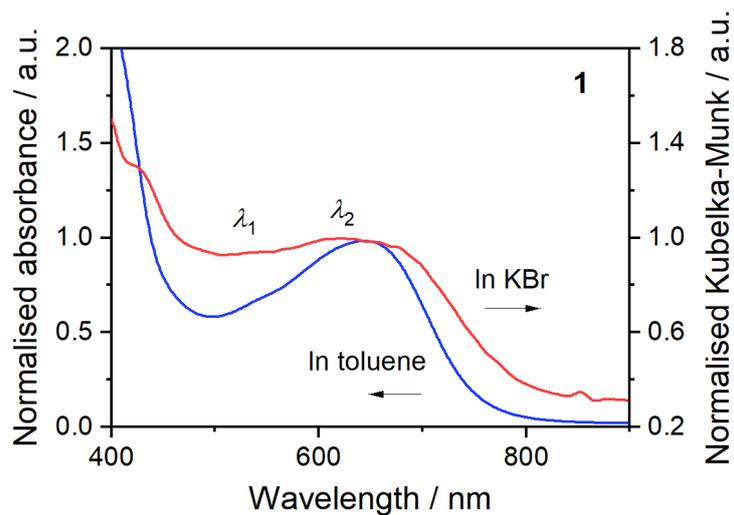


Fig. S11 Comparison of the diffuse reflectance spectrum of **1** (~1% in KBr) with the solution state spectrum in toluene. Both spectra are normalised to the λ_2 transition.

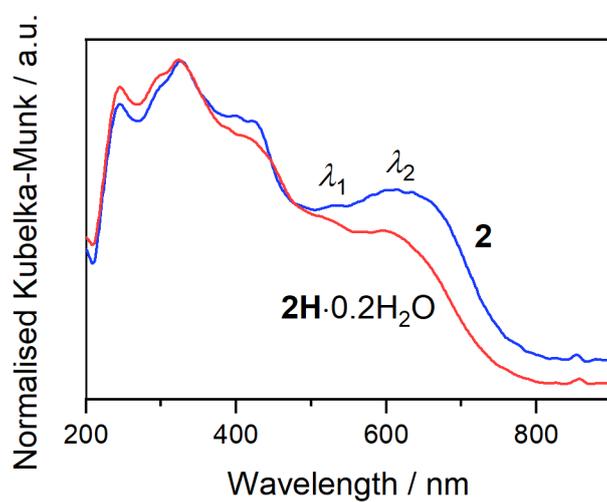


Fig. S12 Diffuse reflectance UV-vis spectra of **2** and **2H·0.2H₂O**, normalised to the highest absorbing peak.

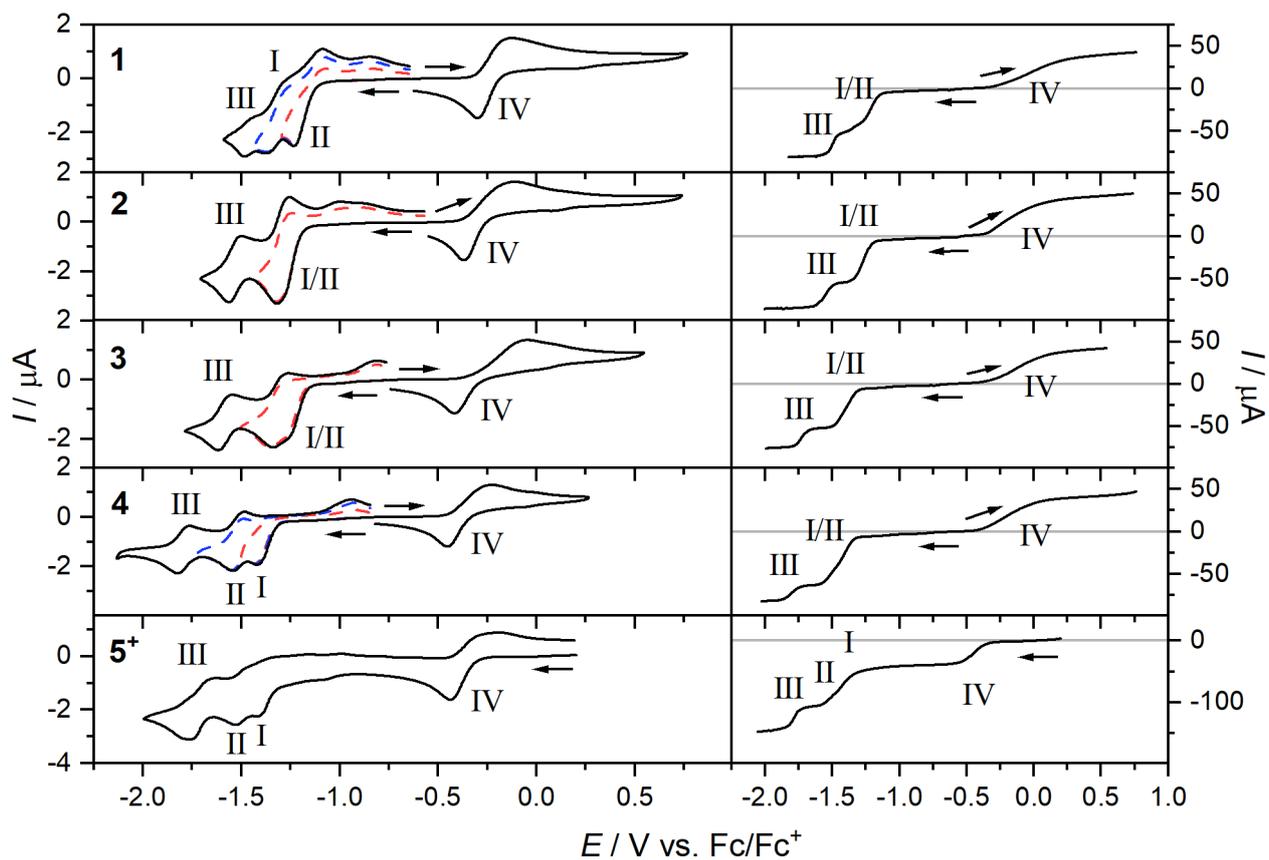


Fig. S13 Cyclic voltammograms of **1–4** and **5⁺** in MeCN (1.0 mM with 0.25 M Bu₄NPF₆) at a scan rate of 100 mV s⁻¹, and RDE voltammograms of **1–4** and **5⁺** (50 mV s⁻¹ scan rate, 500 rpm rotation rate).

Table S3 Cyclic and RDE voltammetry data for compounds **1–4** and **5⁺** in MeCN (1 mM analyte with 0.25 M Bu₄NPF₆).

	Cyclic voltammetry data in V (ΔE in mV)				RDE voltammetry $E_{1/2}$ in V (i_L in μA)		
	<i>I</i> , E_{pc}	<i>II</i> , $E_{1/2}$ (ΔE)	<i>III</i> , $E_{1/2}$ (ΔE)	<i>IV</i> , E_{pa}	<i>I/II</i> ^a	<i>III</i>	<i>IV</i>
1	-1.380	-1.235 ^b	-1.480 ^b	-0.125	-1.261 (46.3)	-1.498 (27.3)	-0.035 (32.8)
2	-1.320 ^a	—	-1.533 (55)	-0.115	-1.270 (46.7)	-1.556 (31.5)	-0.186 (38.1)
3	-1.363 ^a	—	-1.601 (65)	-0.048	-1.401 (46.0)	-1.730 (22.4)	-0.124 (33.2)
4	-1.413	-1.511 (55)	-1.791 (55)	-0.228	-1.442 (56.4)	-1.799 (17.5)	-0.191 (41.8)
5⁺	-1.418	-1.528 ^b	-1.696 (145)	-0.438 ^c	-1.429 (61.3)	-1.785 (33.5)	-0.447 (36.3)

^a E_{pc} or $E_{1/2}$ of the overlapped process combining *I* and *II*. ^b E_{pc} rather than $E_{1/2}$. ^c E_{pc} rather than E_{pa} .

Table S4 Parameters for the linear fits of the solvatochromic shifts of λ_1 and λ_2 to Equation 1 (see main text).

λ_1	c_1	c_2	c_3	R^2
1	2.236	0.246	0.116	0.531
2	2.234	0.373	0.062	0.987
3	2.292	0.199	0.109	0.800
4	2.291	0.153	0.106	0.421
λ_2	c_1	c_2	c_3	R^2
1	1.785	0.293	0.197	0.961
2	1.773	0.358	0.204	0.986
3	1.819	0.349	0.201	0.986
4	1.877	0.098	0.195	0.905

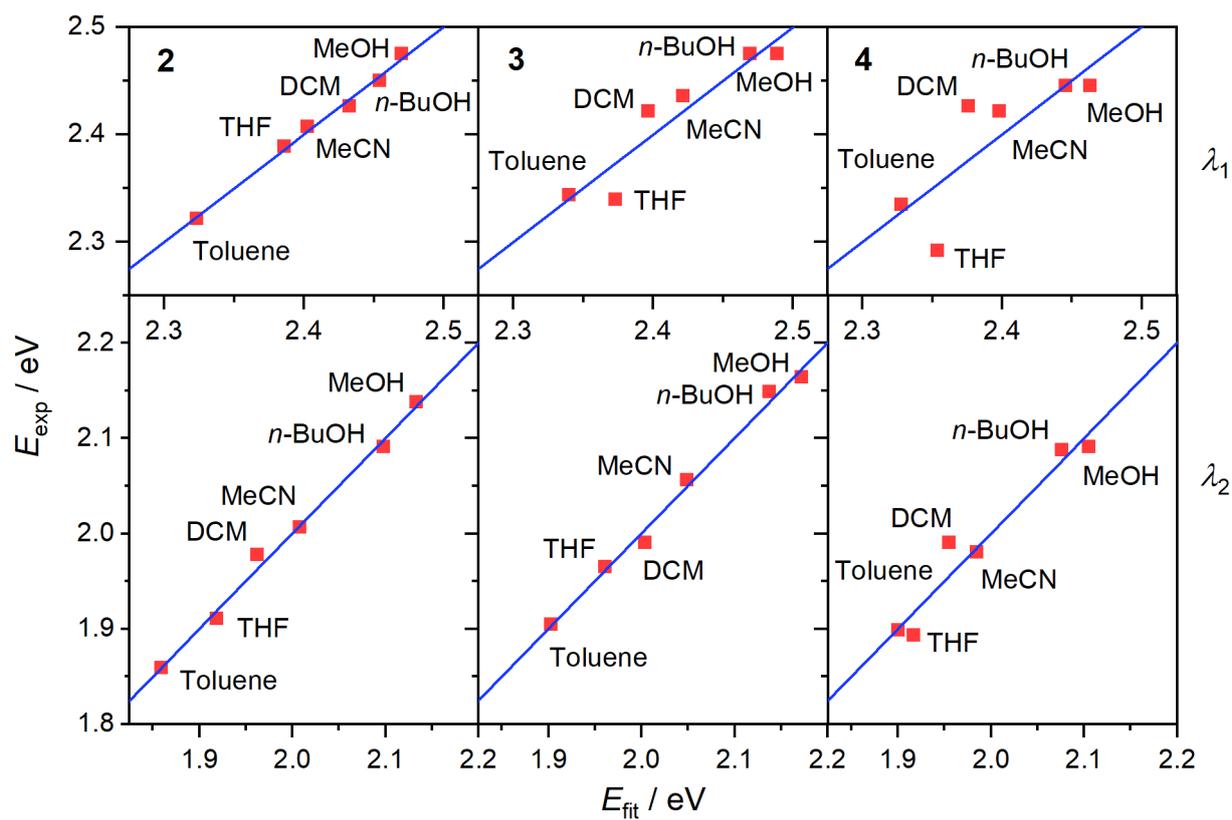


Fig. S14 Experimental excitation energies of the lower energy (top) and higher energy (bottom) visible excitations of **2** (left), **3** (centre), and **4** (right), plotted against the model presented in Eqn. 1 (see text). Fitted parameters presented in Table S3.

References

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- 2 I. L. Fedushkin, A. A. Skatova, V. A. Chudakova and G. K. Fukin, *Angew. Chem., Int. Ed.*, 2003, **42**, 3294–3298.
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