

Electronic Supplementary Information For:

Optical, Third Order Non-Linear Optical and Electrochemical Properties of Dipolar, Centrosymmetric and C_{2v} Organoimido Polyoxometalate Derivatives

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1. Syntheses

Synthesis of (n-Bu₄N)₄[1,4-(Mo₆O₁₈N)₂C₆H₄] (4). A mixture of DCC (1,3-dicyclohexylcarbodiimide) (0.52 g, 2.5 mmol), 1,4-phenylenediamine (0.11 g, 1 mmol) and (n-Bu₄N)₂[Mo₆O₁₉] (3.3 g, 2.4 mmol) was dissolved in DMSO (15 mL). This was stirred and heated to 60 °C for 12 hours. The solution was filtered into diethyl ether (50 mL), producing an oily precipitate. This was washed with several portions of diethyl ether, producing a hard dark red solid. Recrystallization from hot acetonitrile afforded **3** as an orange-brown solid (1.135 g, mmol, 41%). NMR (500 MHz, CD₃CN): δ_H 7.14 (s, 4H, ArH-ortho/meta) 3.10 (*pt*, *J* = 8.6 Hz, 32H), 1.61 (quin, *J* = 8.0 Hz, 32H), 1.36 (*sex*, *J* = 7.4 Hz, 32H), 0.97 (*t*, *J* = 7.4 Hz, 48H). δ_C (125 MHz, CD₃CN); 117.89, 58.92, 23.94, 19.94, 13.42, 0.90. Anal. Calcd (found) % for C₇₀H₁₄₄Mo₁₂N₆O₃₆: C, 30.06 (29.95); H, 5.19 (5.37); N, 3.00 (3.11). *m/z* = 691.3 [Mo₁₂O₃₆N₂C₆H₄(Bu₄N)]³⁻. FTIR (ATR)/cm⁻¹; 975 (Mo=N), 946 (Mo=O). UV-Vis (MeCN) λ, nm (ε, M⁻¹ cm⁻¹): 272 (84.6 × 10³), 425 (69 × 10³).

Synthesis of (n-Bu₄N)₄[1,4-(Mo₆O₁₈N)₂(C₆Me₄)] (5) A mixture of DCC (0.52 g, 2.5 mmol), *N,N,N',N'*-Tetramethyl-*p*-phenylenediamine dihydrochloride (0.164 g, 1 mmol) and (n-Bu₄N)₂[Mo₆O₁₉] (3.3 g, 2.4 mmol) was dissolved in DMSO (15 mL). This was then stirred and heated slowly to 60 °C and left to reflux for 12 hours under argon gas. The solution was filtered into diethyl ether (50 mL). The oily product was then washed again to remove 1,3-dicyclohexylurea (DCU) and other insoluble materials, further drying under vacuum and washings were necessary to get a solid product. This left a hard dark red solid which was recrystallized in hot acetone and left at room temperature for a few days to afford a dark brown solid (0.817 g, 0.286 mmol, 35.8 %) NMR (500 MHz, CD₃CN): δ_H 3.10 (*pt*, *J* = 8.6 Hz, 32H), 2.45 (s, 12H, ArMe-ortho/meta), 1.61 (quin, *J* = 8.0 Hz, 32H), 1.36 (*sex*, *J* = 7.4 Hz, 32H), 0.97 (*t*, *J* = 7.4 Hz, 48H). Anal. Calcd (found) % for C₇₄H₁₅₆Mo₁₂N₆O₃₆: C, 31.10 (31.24); H, 5.50 (5.62); N, 2.94 (3.05). *m/z* = 472.2 [Mo₁₂O₃₆C₁₀H₁₂N₂]⁴⁻, 709.7 [Mo₁₂O₃₆C₂₆H₄₈N₃]³⁻, 1185.7 [Mo₁₂O₃₆C₄₂H₈₄N₄]. FTIR (ATR)/cm⁻¹; 945 (Mo-O), 972 (Mo-N). UV-Vis (MeCN) λ (ε): 440 (61.7 × 10³), 214 (75.7 × 10³).

Synthesis of (n-Bu₄N)₄[1,3-(Mo₆O₁₈N)₂(C₆H₄)] (6). A mixture of DCC (0.52 g, 2.5 mmol), 1,3-phenylenediamine (0.11 g, 1 mmol) and (n-Bu₄N)₂[Mo₆O₁₉] (3.3 g, 2.4 mmol) was dissolved in DMSO (15 mL). This was then stirred and heated slowly at 60 °C for 17 hours. The solution was filtered into diethyl ether (50 mL), producing an oily precipitate. This was triturated several times with diethyl ether and dried *in vacuo* between washings, until a hard dark red solid was obtained. Recrystallization from hot acetone afforded **4** as an orange-brown solid (1.914 g, 0.68 mmol, 68 %) NMR (500 MHz, CD₃CN): δ_H 7.44 (*t*, 1H, ArH-meta), 7.15 (*dd*, 2H, ArH-ortho), 6.92 (*s*, 1H, ArH-para) 3.10 (*pt*, *J* = 8.6 Hz, 32H), 1.61 (quin, *J* = 8.0 Hz, 32H), 1.36 (*sex*, *J* = 7.4 Hz, 32H), 0.97 (*t*, *J* = 7.4 Hz, 48H). δ_C (125 MHz, CD₃CN); 118.06, 58.92, 24.01, 19.97, 13.47, 0.896. Anal. Calcd (found) % for C₇₀H₁₄₄Mo₁₂N₆O₃₆: C, 30.06 (30.07); H, 5.19 (5.21); N, 3.00 (3.06). *m/z* = 691.7 [Mo₁₂O₃₆N₂C₆H₄(Bu₄N)]³⁻. FTIR (ATR)/cm⁻¹; 976 (Mo=N), 945 (Mo=O). UV-Vis (MeCN) λ, nm (ε, M⁻¹ cm⁻¹): 258 (81.6 × 10³), 348 (55.5 × 10³).

Synthesis of (n-Bu₄N)₄[1,3-(Mo₆O₁₈)₂(C₆HMe₃)] (7). A mixture of DCC (0.52 g, 2.5 mmol), 2,4,6-trimethyl-m-phenylenediamine (0.152 g, 1 mmol) and (n-Bu₄N)₂[Mo₆O₁₉] (3.3 g, 2.4 mmol) was dissolved in DMSO (15 mL). This was then stirred and heated slowly to 60 °C and left to reflux for 12 hours under argon gas. The solution was filtered into diethyl ether (50 mL). The oily product was then washed again to remove DCU and other insoluble materials, further drying under vacuum and washings were necessary to get a solid product. This left a hard dark red solid which was recrystallized in hot acetonitrile. Further addition of diethyl ether was required to recrystallize afford an orange solid (1.156 g, 0.407 mmol, 40.7 %) NMR (500 MHz, CD₃CN): δ_H 6.92 (s, 1H, ArH-meta), 3.10 (pt, *J* = 8.6 Hz, 32H), 2.93 (s, 6H, ArMe-o ortho/para), 2.63 (s, 3H, ArMe-ortho), 1.62 (quin, *J* = 8.0 Hz, 32H), 1.37 (sex, *J* = 7.4 Hz, 32H), 0.96 (t, *J* = 7.4 Hz, 48H). Anal. Calcd (found) % for C₇₃H₁₅₄Mo₁₂N₈O₃₆: C, 30.83 (30.95); H, 5.46 (5.57); N, 2.96 (3.03). FTIR (ATR)/cm⁻¹; 947 (Mo-O), 974 (Mo-N). UV-Vis (MeCN) λ (ε): 361 (49.1 × 10³), 257 (68.0 × 10³).

2. X-ray Crystallographic Details

Table S1 X-ray Crystallographic Data and Refinement Details for **4•2MeCN**

Formula	C ₇₄ H ₁₅₄ Mo ₁₂ N ₈ O ₃₆
<i>M</i>	2883.32
cryst syst	Triclinic
space group	<i>P</i> -1
<i>a</i> /Å	11.5075(4)
<i>b</i> /Å	12.0506(6)
<i>c</i> /Å	19.3113(10)
<i>α</i> /deg	76.208(5)
<i>β</i> /deg	84.833(4)
<i>γ</i> /deg	85.902(3)
<i>U</i> /Å ³	2586.7(2)
<i>Z</i>	1
<i>T</i> /K	140(2)
<i>μ</i> /mm ⁻¹	1.480
Cryst. size/mm	0.20 × 0.20 × 0.05
Cryst. description	Orange plate
<i>λ</i> /Å	0.71073
No. reflns collected	22102
No. of indep. reflns (<i>R</i> _{int})	11733 [<i>R</i> (int) = 0.1114]
<i>θ</i> _{max} /deg (completeness)	25.00 (98.8%)
Reflections with <i>I</i> > 2σ(<i>I</i>)	4619
Goodness-of-fit on <i>F</i> ²	0.966
final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^a	<i>R</i> 1 = 0.0877, <i>wR</i> 2 = 0.1432
(all data)	<i>R</i> 1 = 0.2043, <i>wR</i> 2 = 0.1946
Peak and hole/e Å ⁻³	1.832 and -1.273

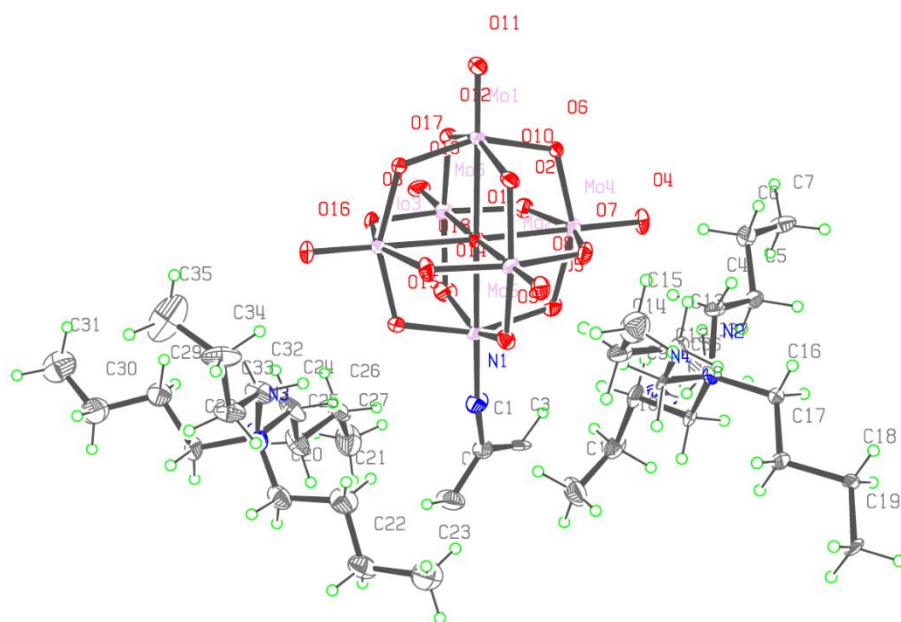


Figure S1 The asymmetric unit of **4•2MeCN**. Thermal ellipsoids are at the 30% probability level. Mo atoms are coloured purple; C, grey; O, red; N, blue; H atoms are represented by green circles of arbitrary radii.

3. Additional Electronic Absorption Spectra

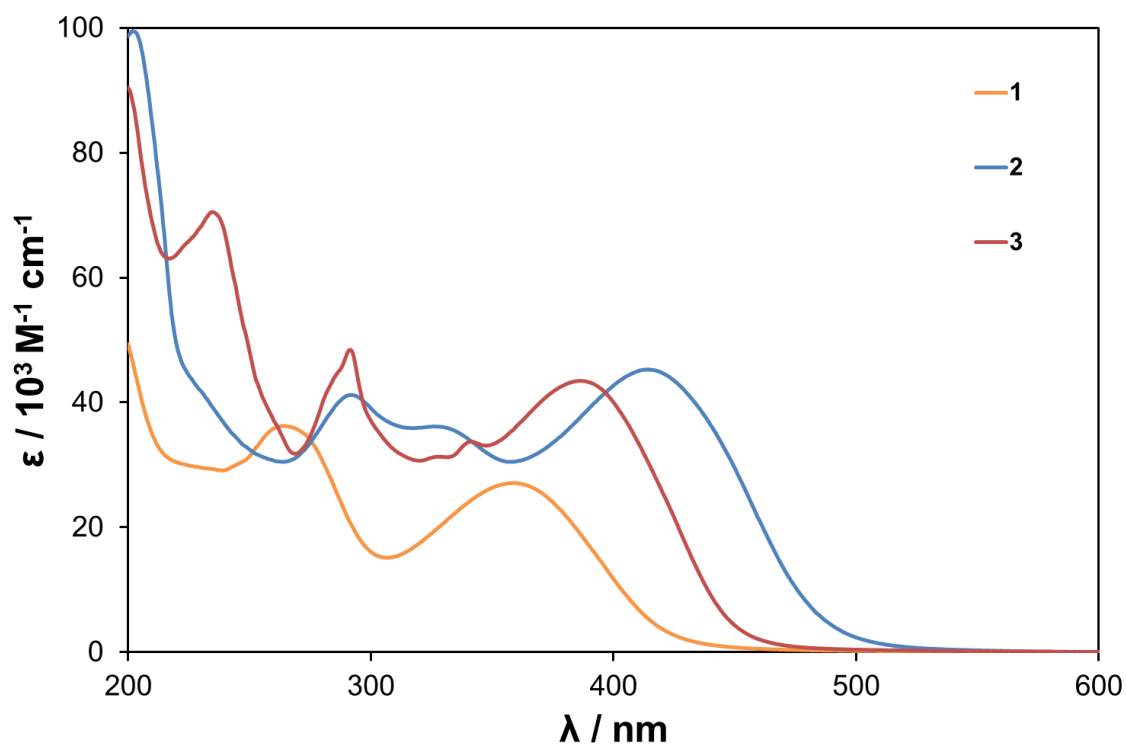


Figure S2 UV-vis absorption spectra of dipolar hexamolybdate derivatives **1** to **3**.

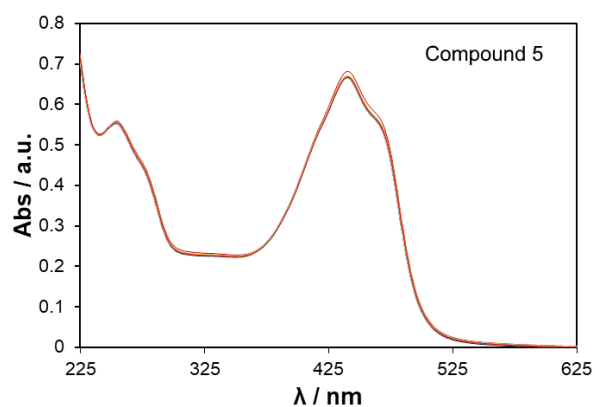
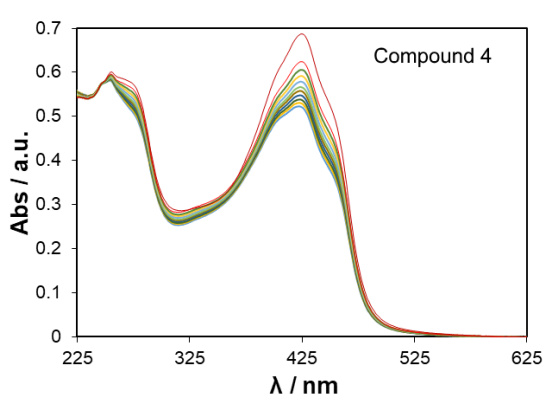
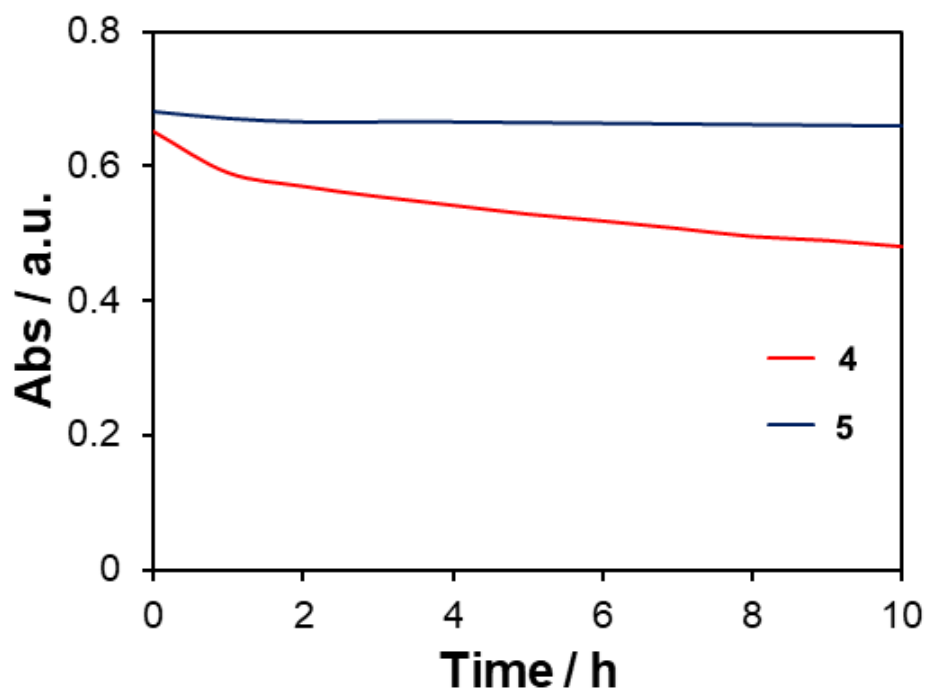


Figure S3 Top: Declines in UV-vis absorbance over time for compounds **4** and **5**, monitored over 10 hours after adding a single drop of water to a 3 mL UV-vis cuvette. **Bottom:** Evolution of the underlying spectra over 10 hours after addition of water. The concentrations of **4** and **5** are *ca.* 10^{-5} M.

4. Cyclic Voltammograms and Deconvolution of Differential Pulsed Voltammetry

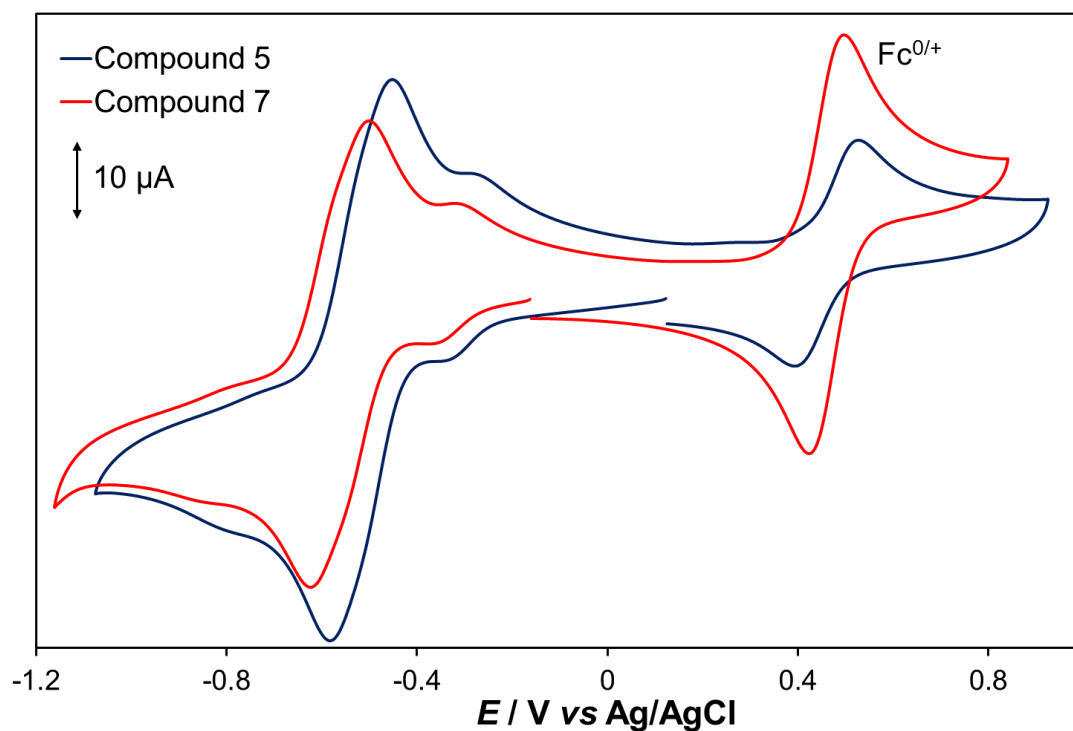


Figure S4 Cyclic voltammograms of **5** and **7** recorded at 100 mV s^{-1} in $0.1 \text{ M } [\text{NBu}_4][\text{BF}_4]$ in acetonitrile. The small peaks close to -0.4 V are from $[\text{Mo}_6\text{O}_{19}]^{2-}$ impurities.

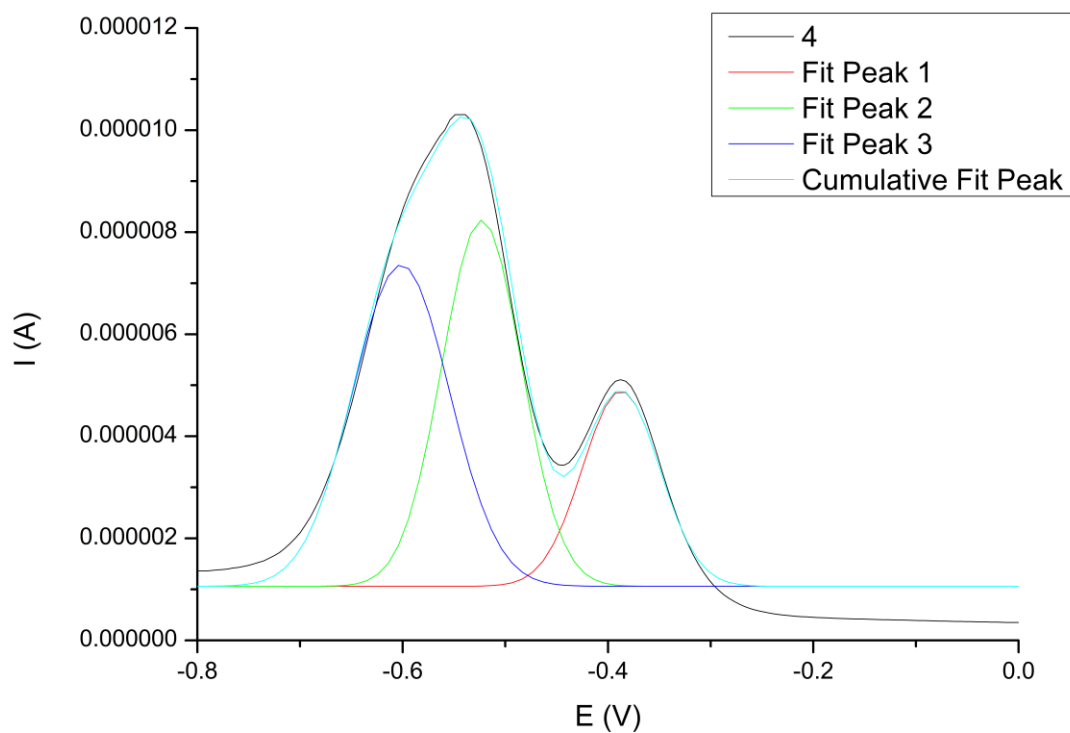


Figure S5 Deconvolution of the differential pulsed voltammogram of **4**.

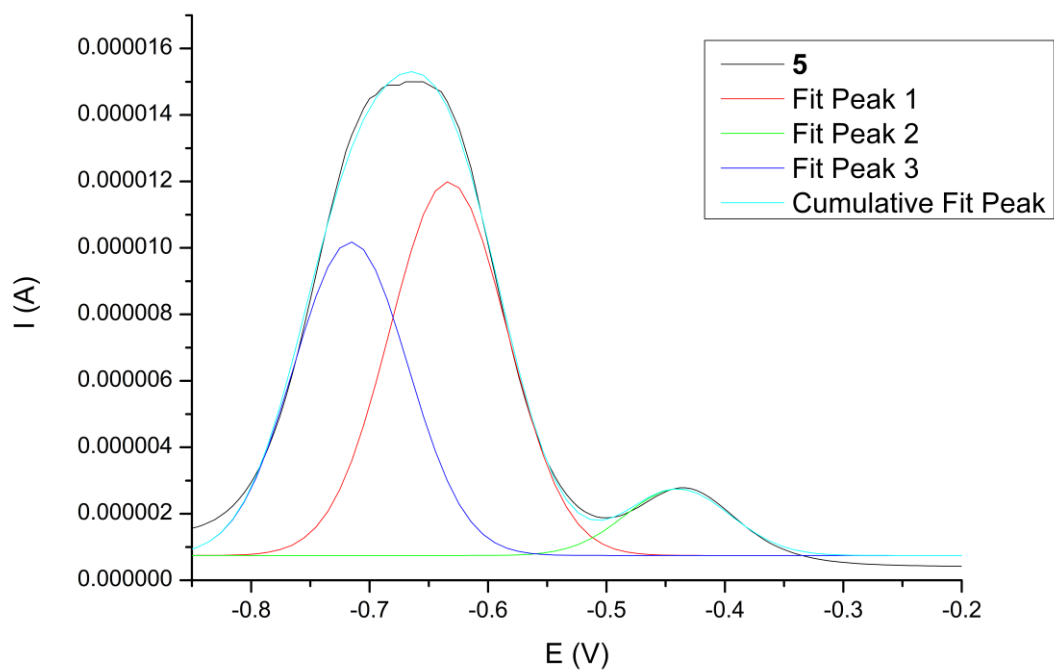


Figure S6 Deconvolution of the differential pulsed voltammogram of **5**

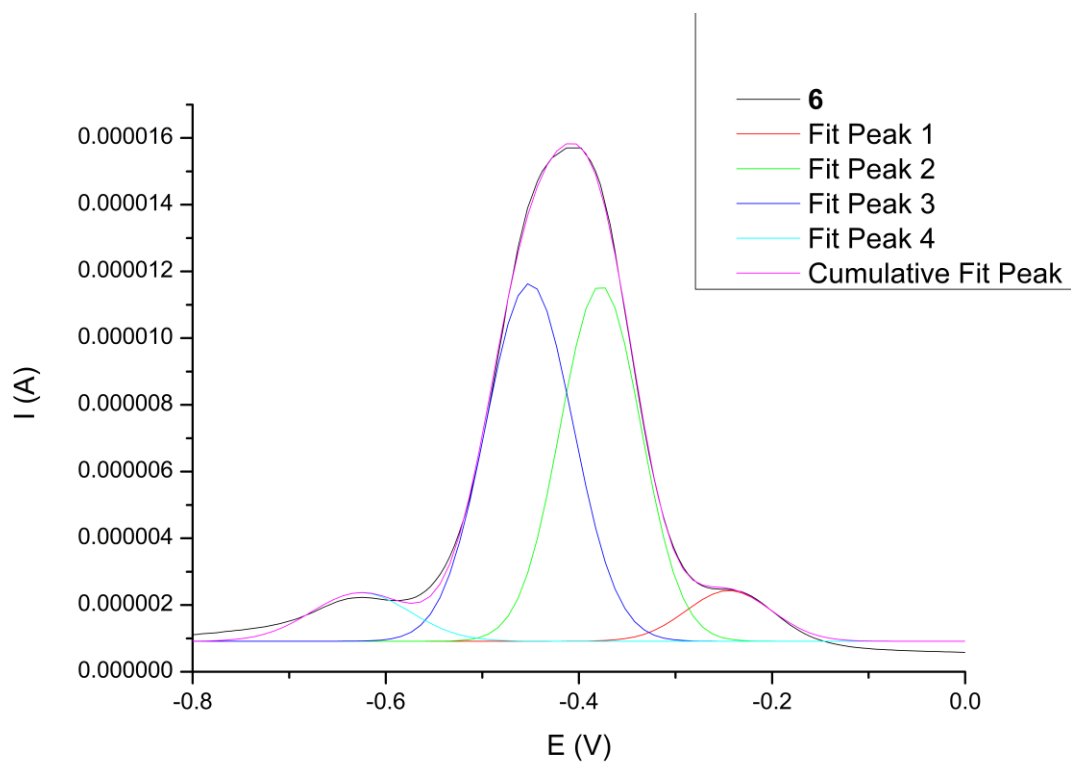


Figure S7 Deconvolution of the differential pulsed voltammogram of **6**

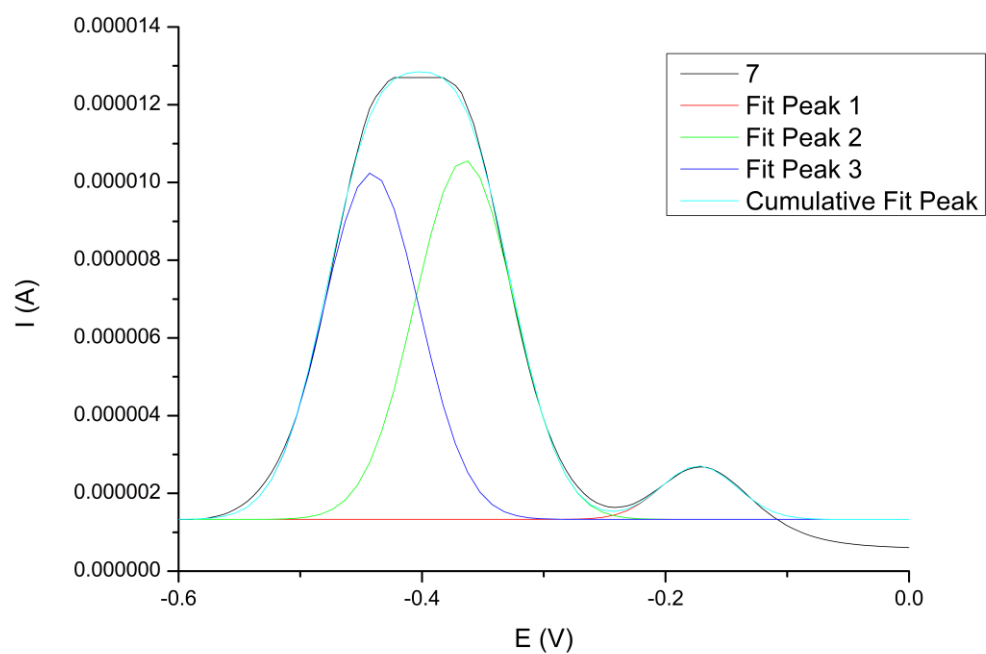


Figure S8 Deconvolution of the differential pulsed voltammogram of **7**.

3. Z-Scan Data

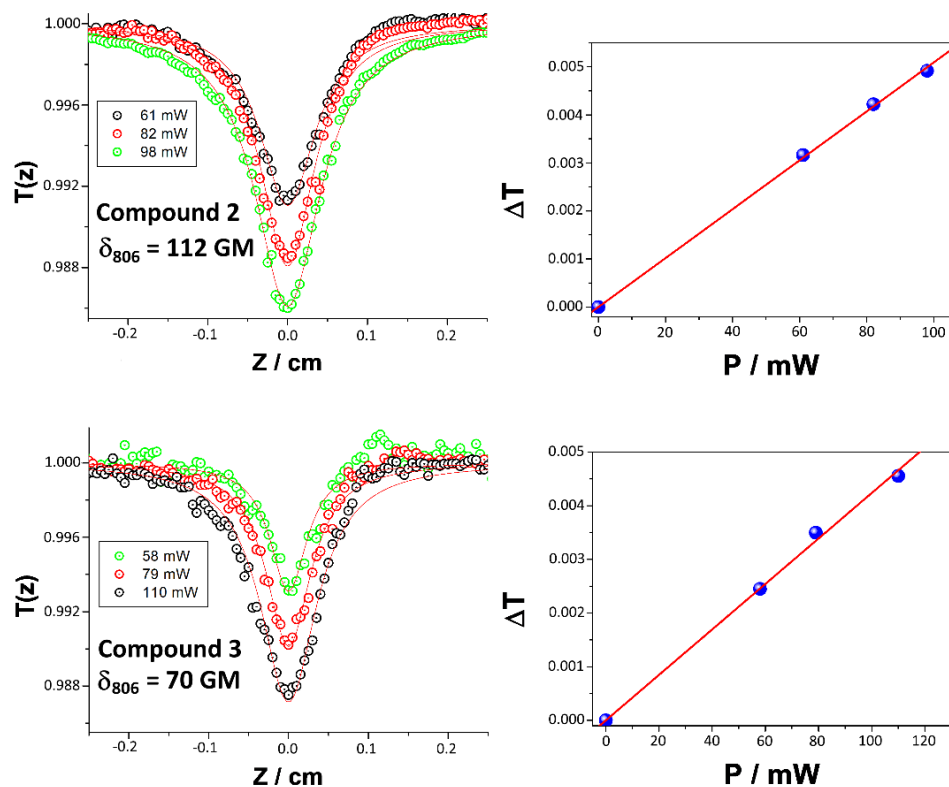


Figure S9 Z-scan data curves (circles) and fits (solid lines) for dipolar compounds 2 and 3 (left) and corresponding plots of power versus change in transmittance (right). The non-linear absorbance of compound 1 was too weak to measure accurately.

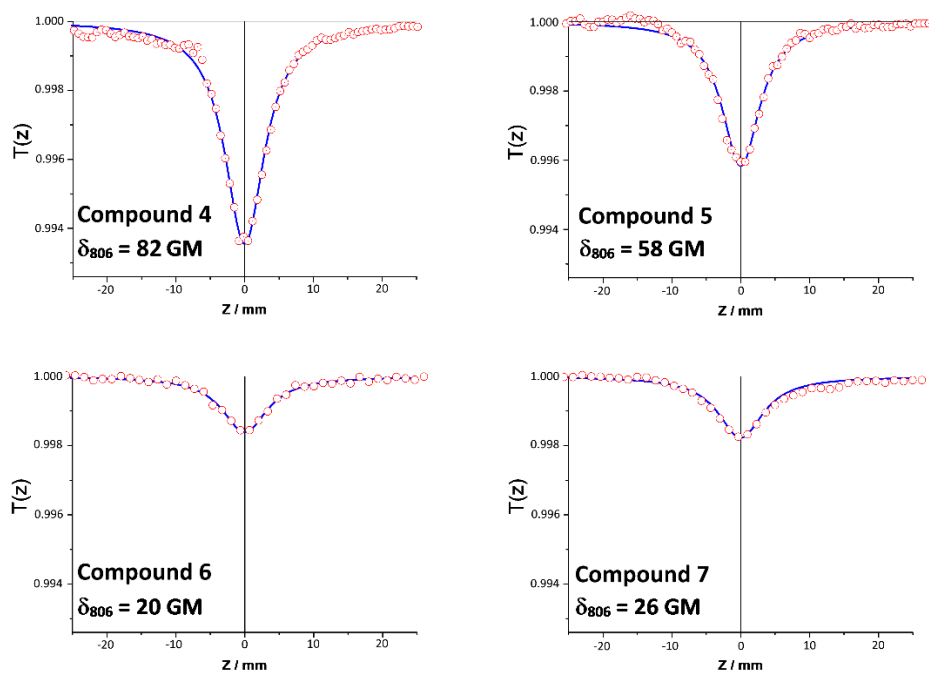


Figure S10 Z-scan data curves (circles) and fits (solid lines) for centrosymmetric compounds 4 to 7.

4. Additional Computational Data

Table S2: Effects of the exchange-correlation functional and basis set on selected equilibrium bond lengths (Å) and angles (°) of compound **4**. Calculations were performed in the gas phase.

Functional /Basis set	Mo-N-C	Mo-N	N-C	Mo-O _c ^a
BP86/6-31G/SSD	180	1.78	1.37	2.27
μB97XD/6-31G/SDD	180	1.73	1.38	2.26
BP86/def2TZVP	180	1.77	1.36	2.23
BP86/6-31G/LanL2DZ	180	1.79	1.37	2.26
ωB97XD/6-311+G(d,p) /LanL2DZ	172	1.73	1.37	2.23
ωB97XD/6-311+G(d,p) /LanL2TZ	174.6	1.73	1.37	2.24
Exp.	160.8	1.714	1.43	2.21

^aCentral oxygen

Table S3. Selected, calculated geometric parameters for **2** and **3** at the ωB97XD/6-311+G(d,p) /LanL2DZ level of theory.

Compound	Mo≡N-C	Mo-N	N-C	Mo-O _c ^a	Mo=O
2	154.2	1.76	1.36	2.18	1.69
3	158.7	1.79	1.34	2.19	1.71

^aCentral oxygen

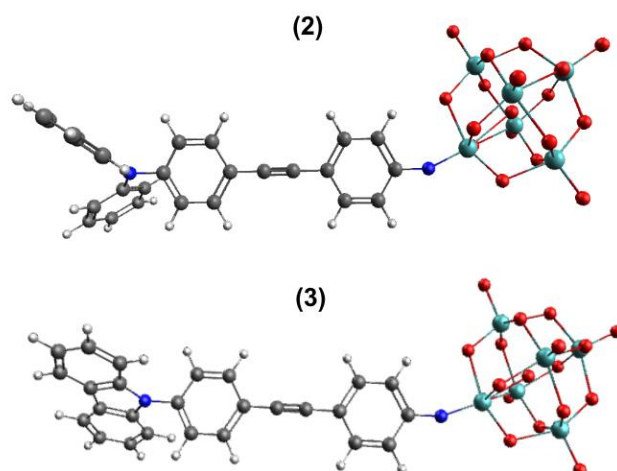


Figure S11: Calculated geometries of **2** and **3** at the ωB97XD/6-311+G(d,p) /LanL2DZ level of theory.

Table S4: Electronic transitions of **2** and **3** calculated at the the ω B97XD/6-311+G(d,p) /LanL2DZ level of theory.

Compound	Experimental		Calculated				
	$\lambda_{\text{max}} / \text{nm}$	$E_{\text{max}} / \text{eV}$	$\lambda_{\text{max}} / \text{nm}$	$E_{\text{max}} / \text{eV}$	f_{os}	Transition	Contr. %
2	414	2.98	444	2.789	0.101	HOMO \rightarrow LUMO+1	15
						HOMO \rightarrow LUMO+6	13
						HOMO \rightarrow LUMO+7	6
			HOMO \rightarrow LUMO+10	13			
			363	3.420	2.055	HOMO-1 \rightarrow LUMO	65
HOMO-2 \rightarrow LUMO	11						
3	385	3.20	382	3.25	1.889	HOMO-1 \rightarrow LUMO	80

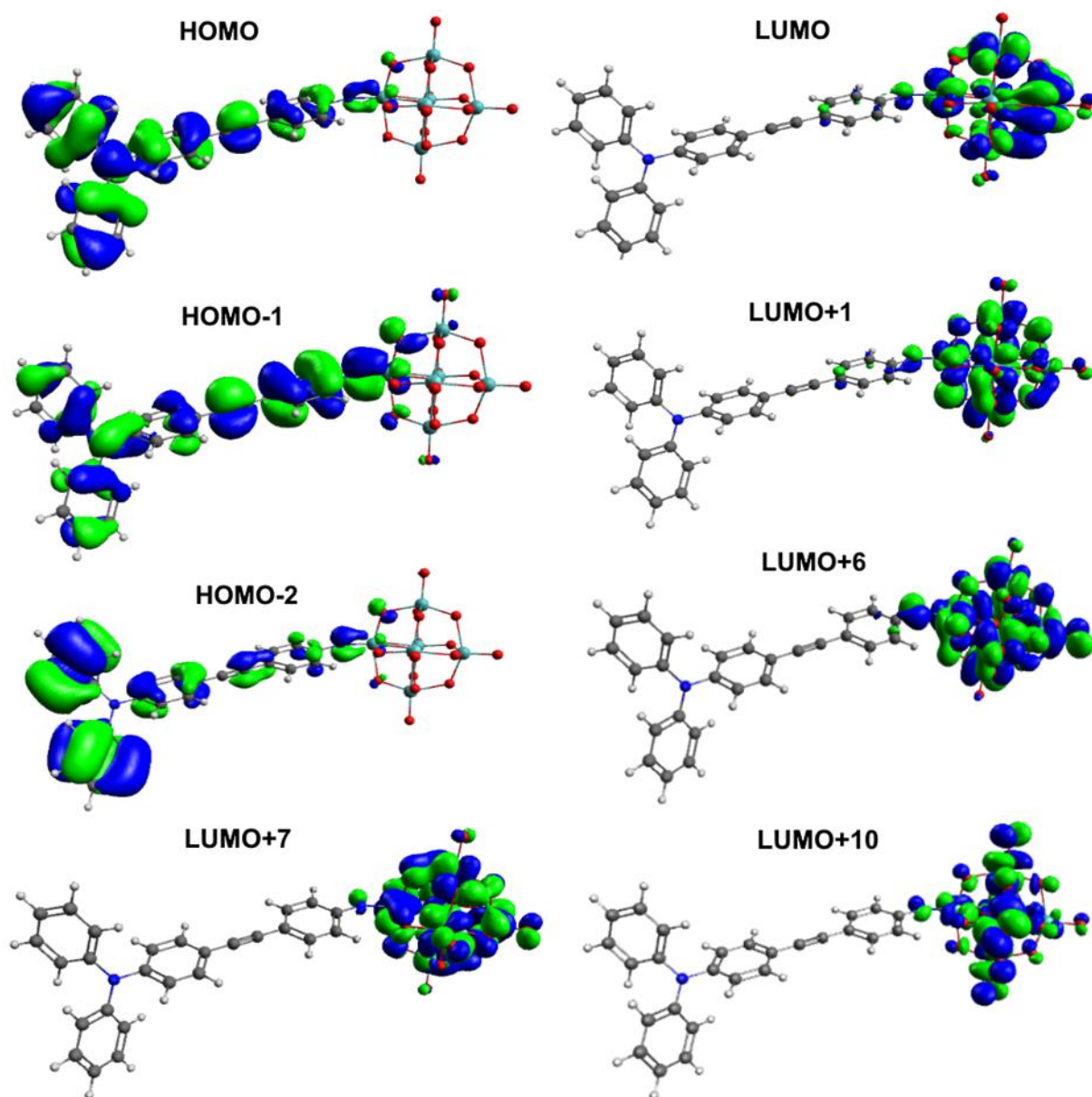


Figure S12. Solvent phase frontier orbitals involved in the significant UV-vis transitions of 2.

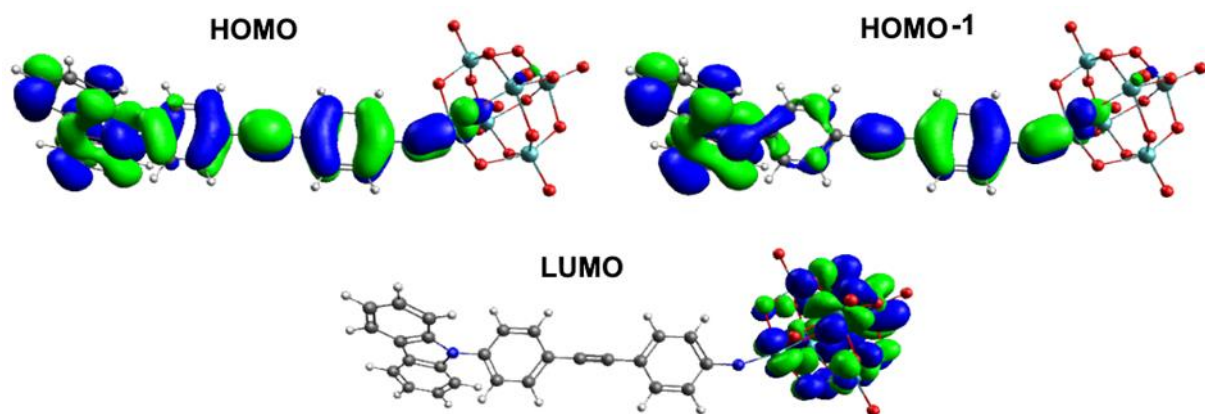


Figure S13. Solvent phase frontier orbitals involved in the significant UV-vis transitions of 3.

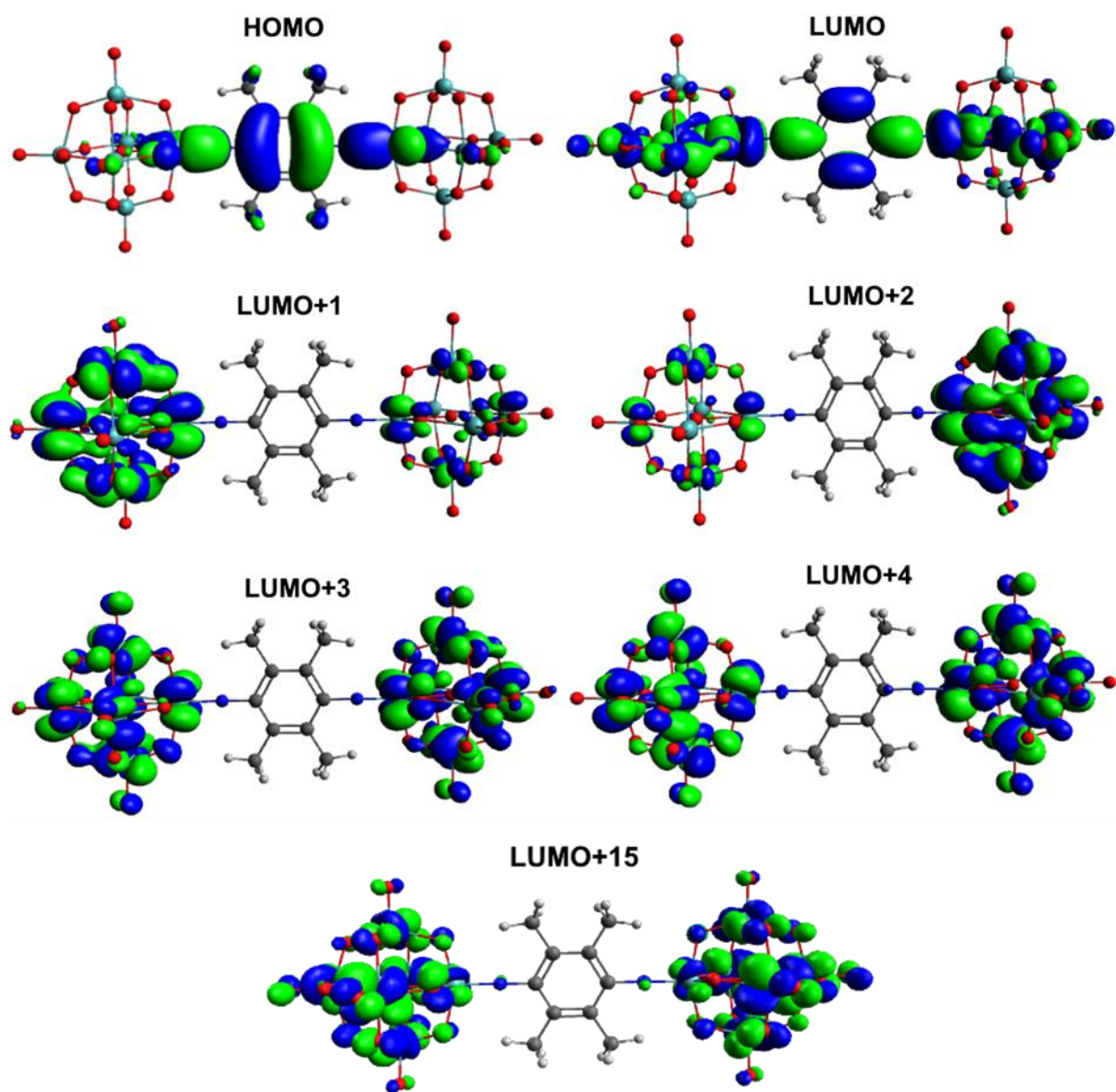


Figure S14. Solvent phase frontier orbitals involved in the significant UV-vis transitions of **5**.

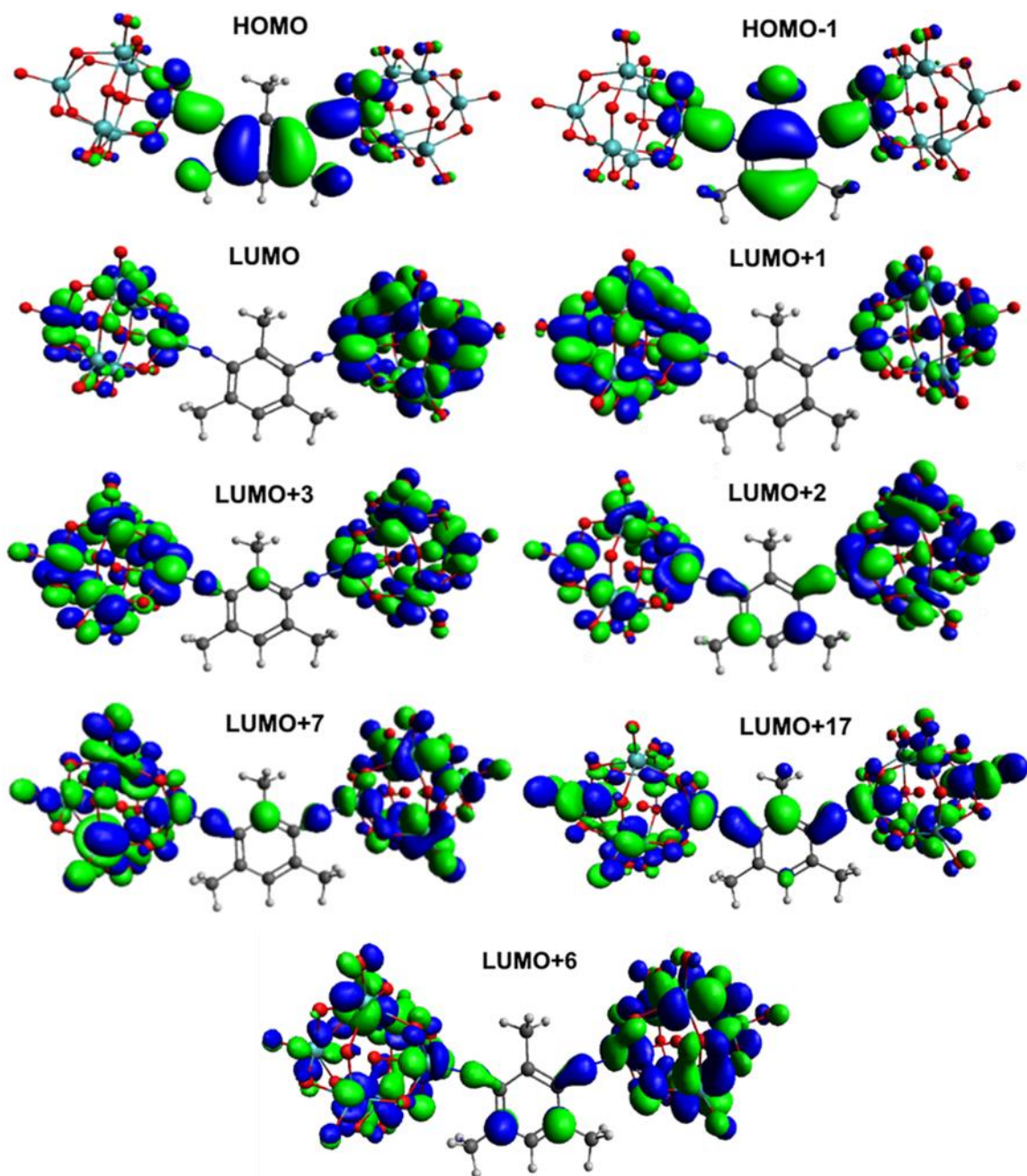


Figure S15. Solvent phase frontier orbitals involved in the significant UV-vis transitions of **7**.

Table S5. Experimental and Calculated Electronic Transitions of Compounds **7** at the ω B97X-D and CAM-B3LYP/6-311+G(d,p)/LanL2DZ level of theory.

		ω B97X-D		CAM-B3LYP				
	Exp. λ_{\max}/nm	E_{\max}/eV	λ_{\max}/nm	E_{\max}/eV	λ_{\max}/nm	f_{os}	Transition	Contr.
7	361	3.3826	366.54	3.2725	378.86	1.2952	HOMO \rightarrow LUMO+1	0.12132
							HOMO \rightarrow LUMO+6	0.30076
							HOMO \rightarrow LUMO+9	0.20317
		3.4230	362.21	3.3276	372.60	0.1104	HOMO \rightarrow LUMO	0.13772
							HOMO \rightarrow LUMO+3	0.12925
							HOMO \rightarrow LUMO+7	0.31049
							HOMO \rightarrow LUMO+16	0.24494