

Tuning supramolecular aurophilic structures: the effect of couterion, positive charge and solvent

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Supplementary Material

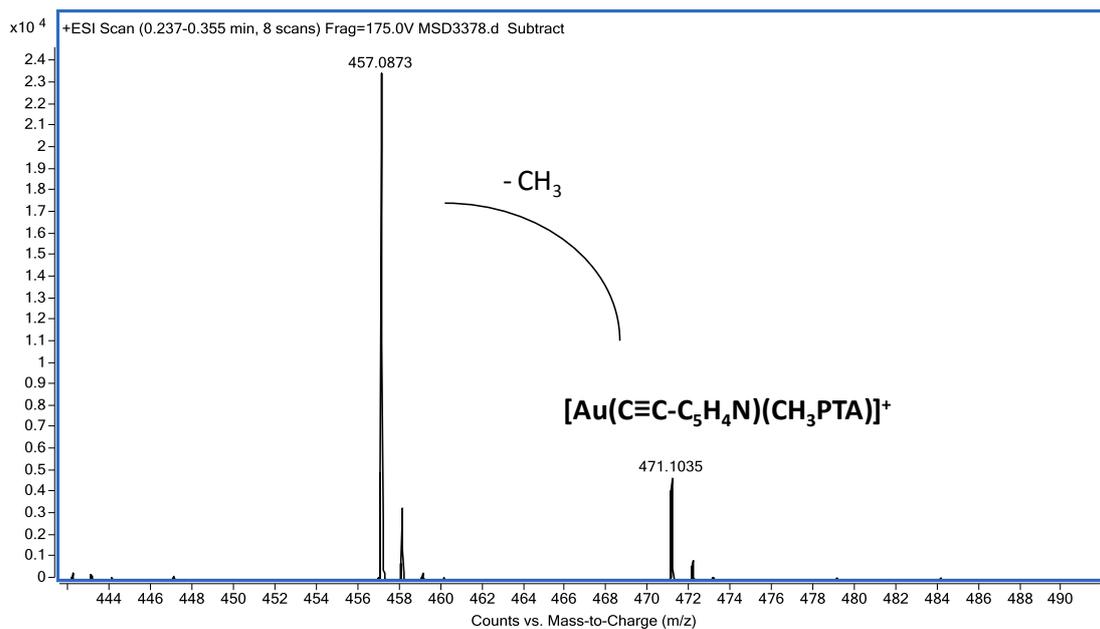


Figure S1. HR-ESI(+) mass spectrum of complex 1.

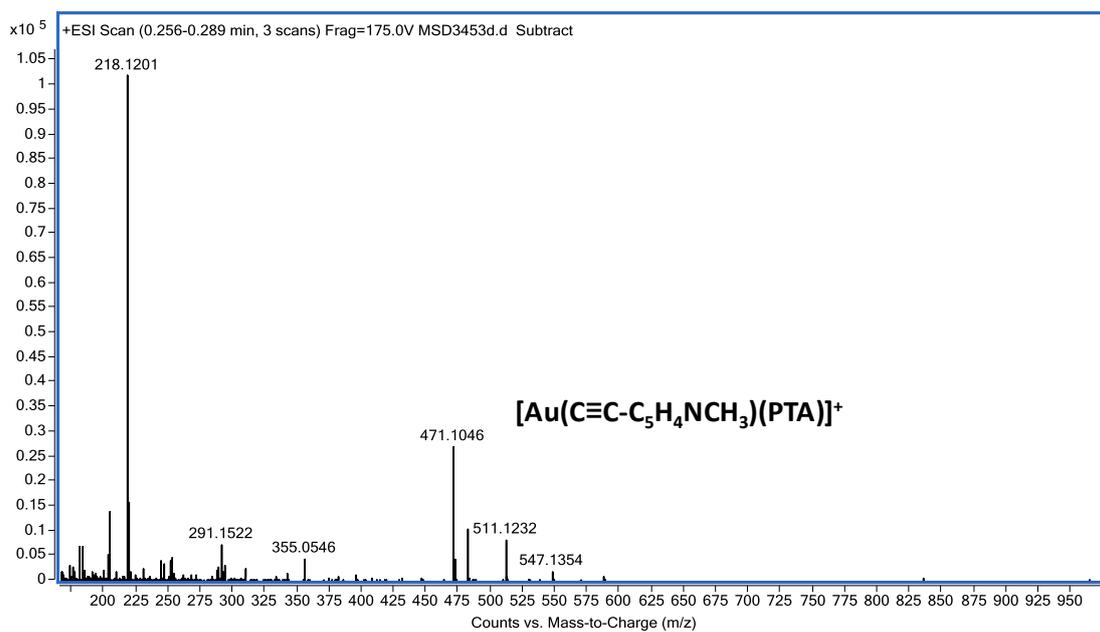


Figure S2. HR-ESI(+) mass spectrum of complex 2.

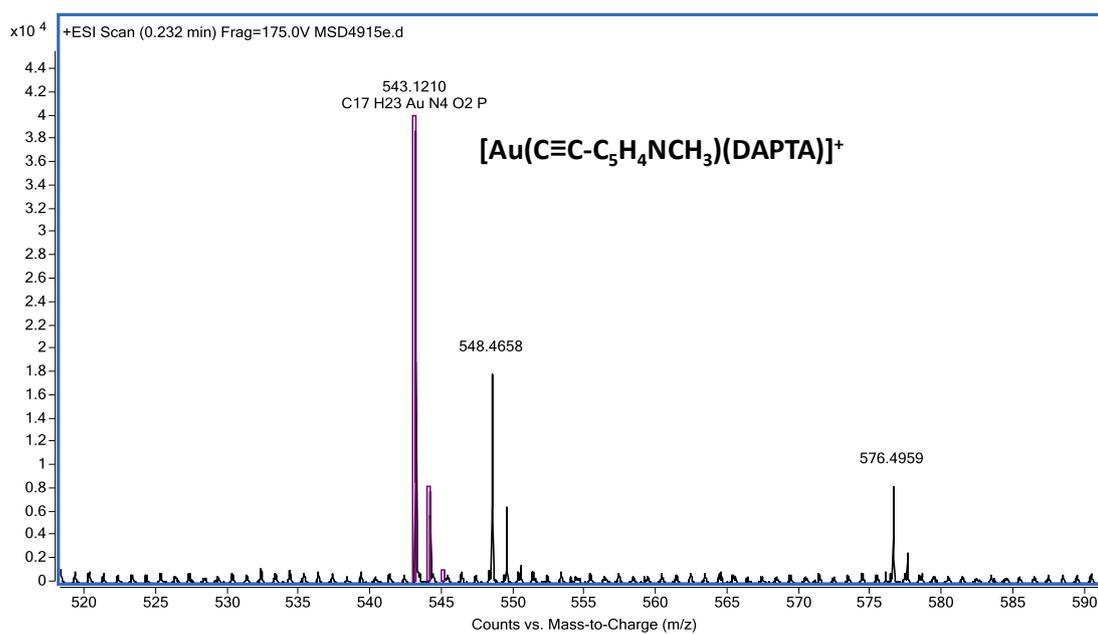


Figure S3. HR-ESI(+) mass spectrum of complex **3**.

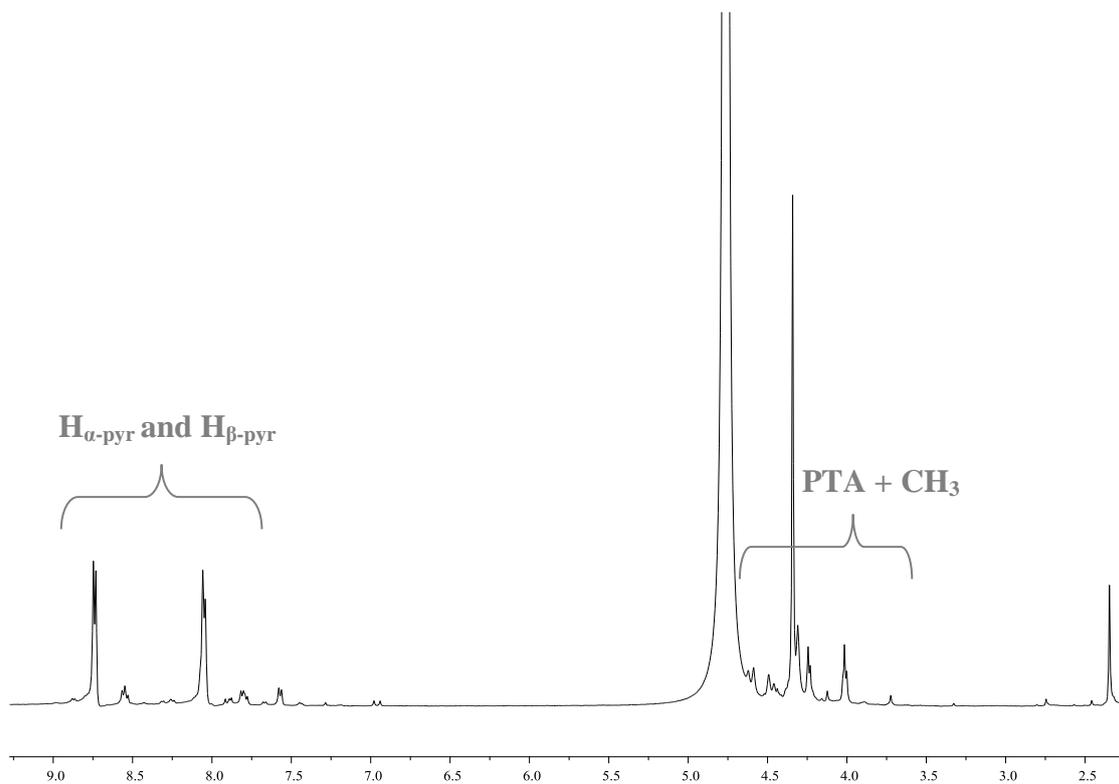


Figure S4. ¹H-NMR spectrum of **2** in D₂O.

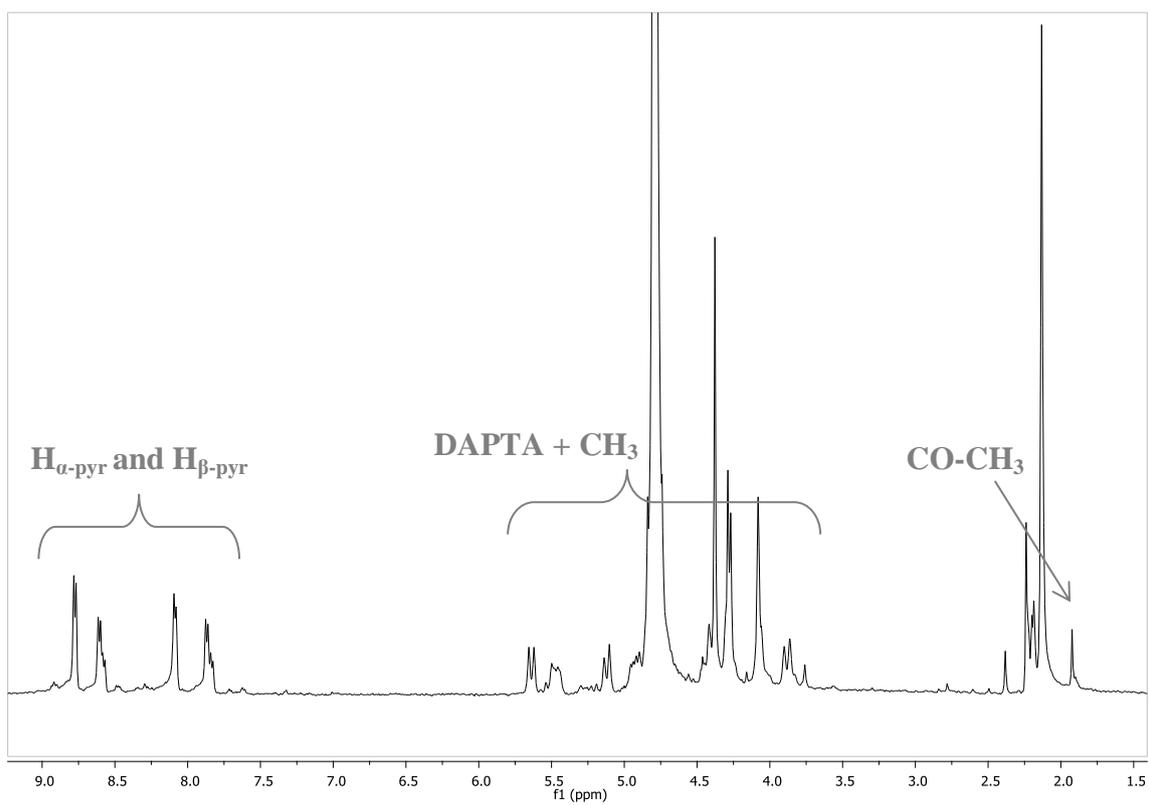


Figure S5. $^1\text{H-NMR}$ spectrum of **3** in D_2O .

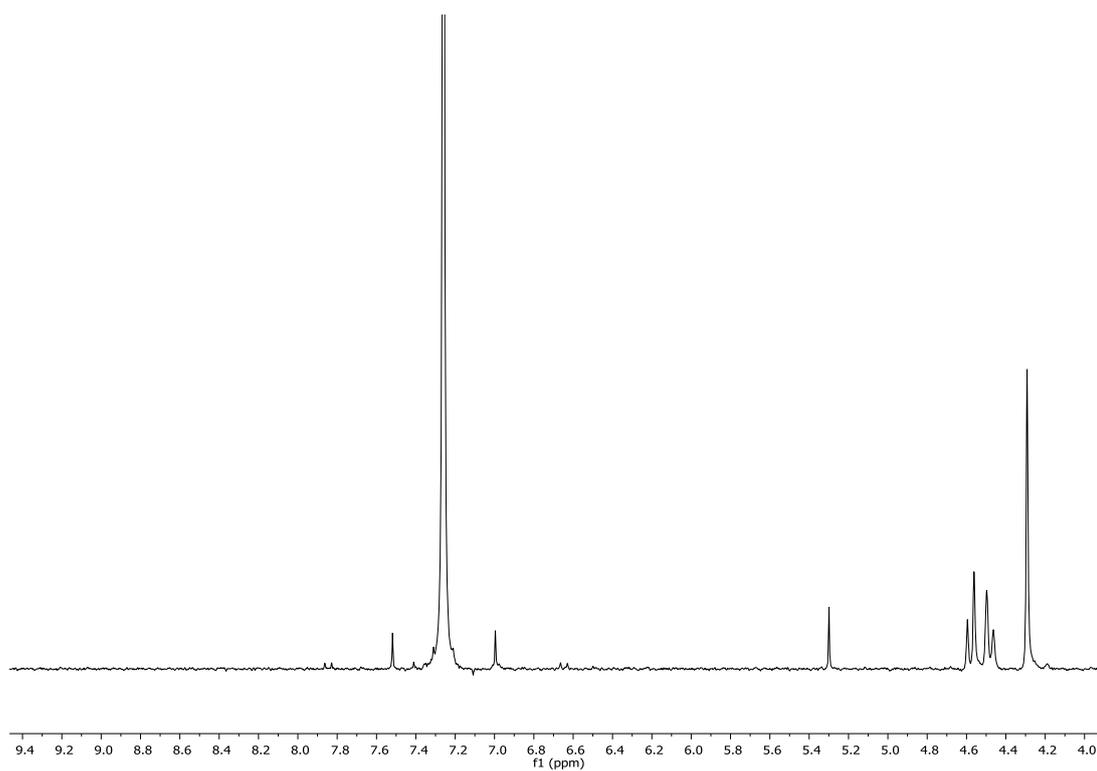


Figure S6. $^1\text{H-NMR}$ spectrum of **2** in CDCl_3 .

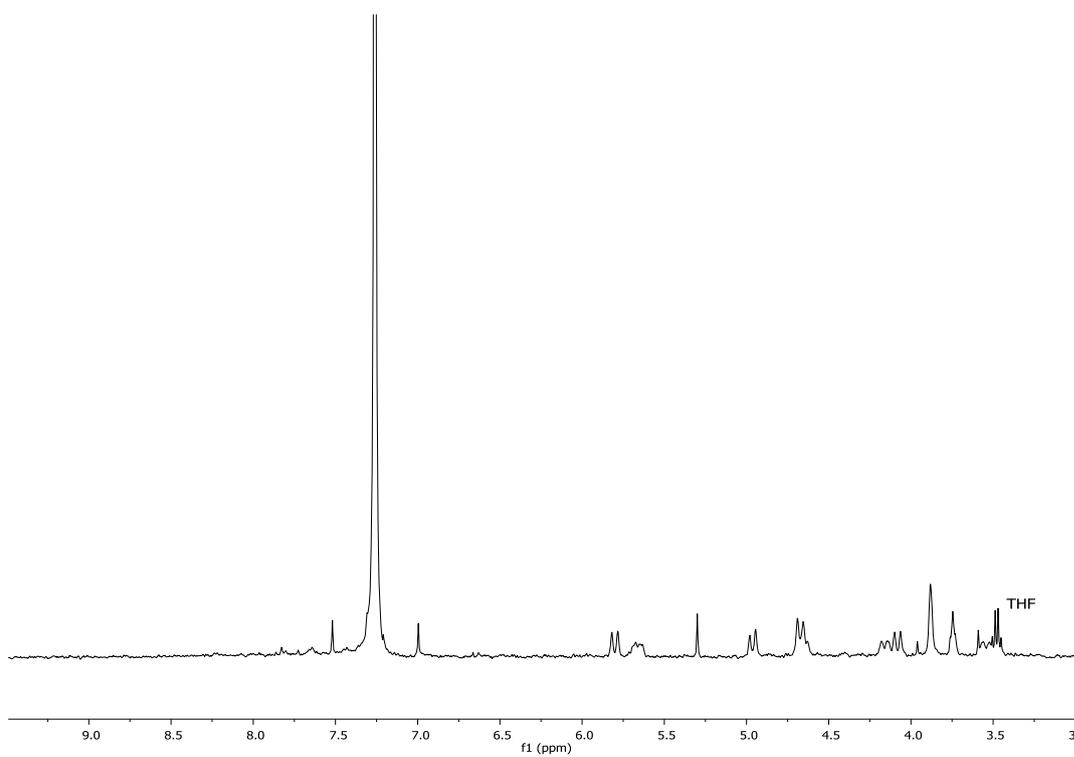


Figure S7. $^1\text{H-NMR}$ spectrum of **3** in CDCl_3 .

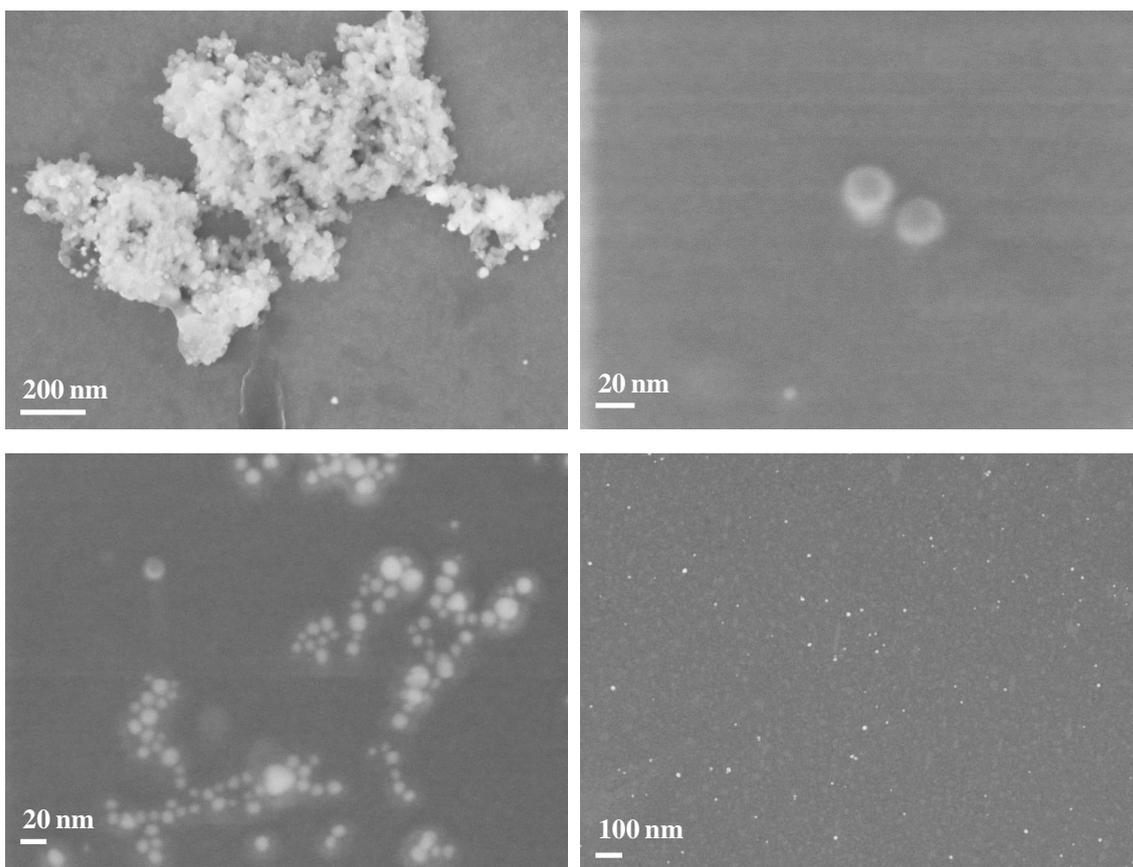


Figure S8. SEM images of dried samples of **2** (up) and **3** (bottom).

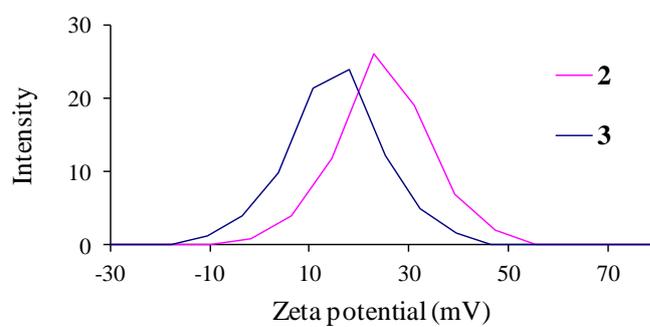


Figure S9. Z potential values measured for 5×10^{-5} M solutions of **2** and **3** in water by DLS measurements.

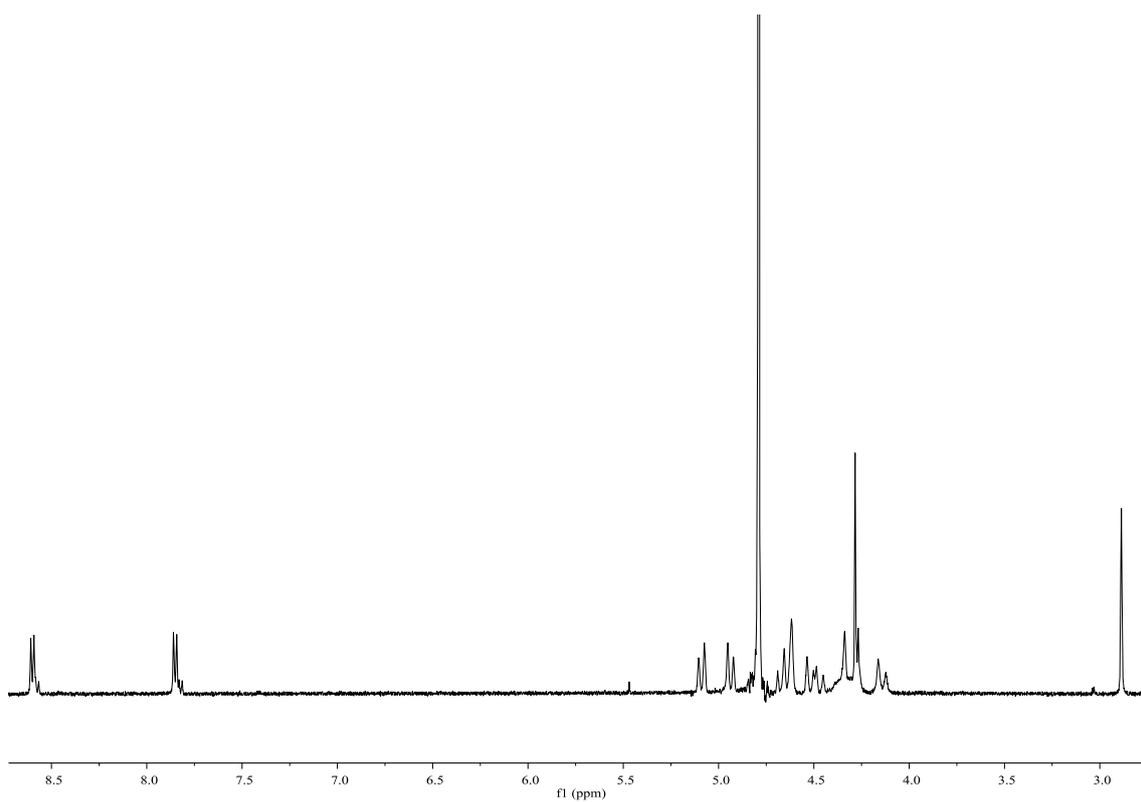


Figure S10. $^1\text{H-NMR}$ spectrum **4** in water.

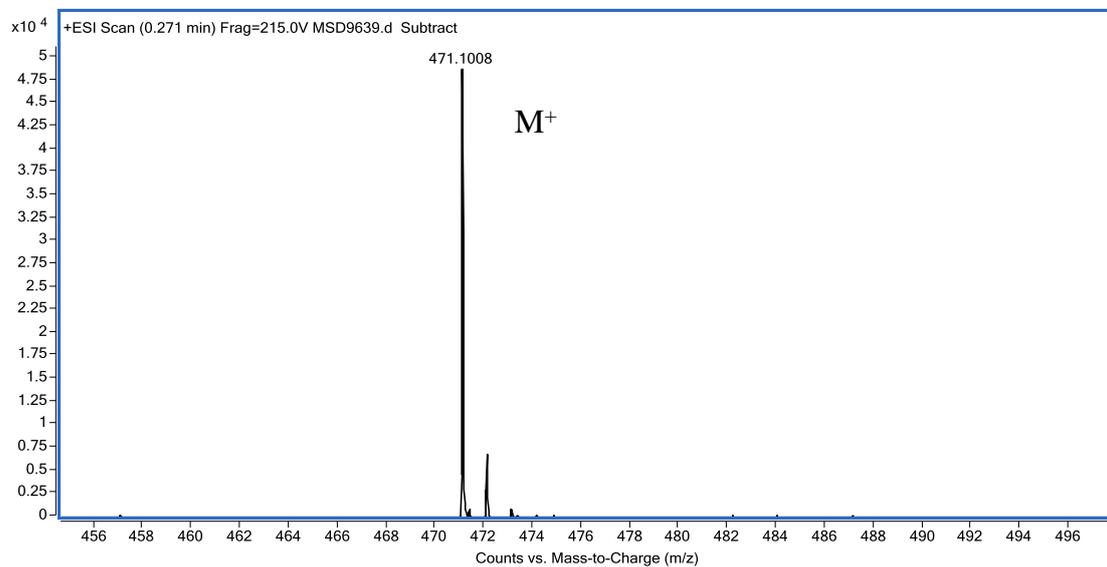


Figure S11. HR-ESI(+) mass spectrum of complex **5**.

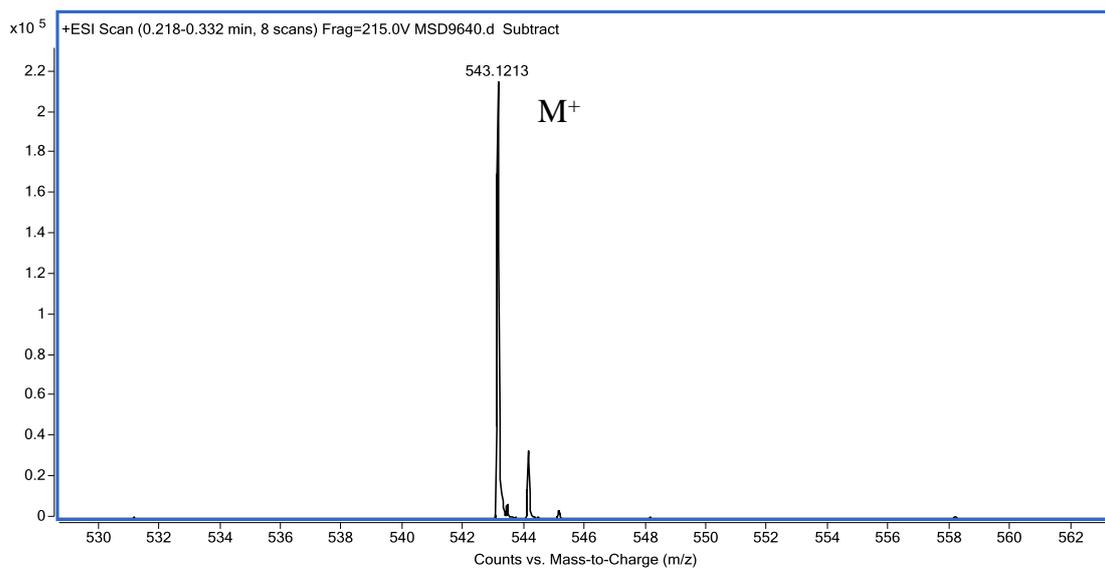


Figure S12. HR-ESI(+) mass spectrum of complex **6**.

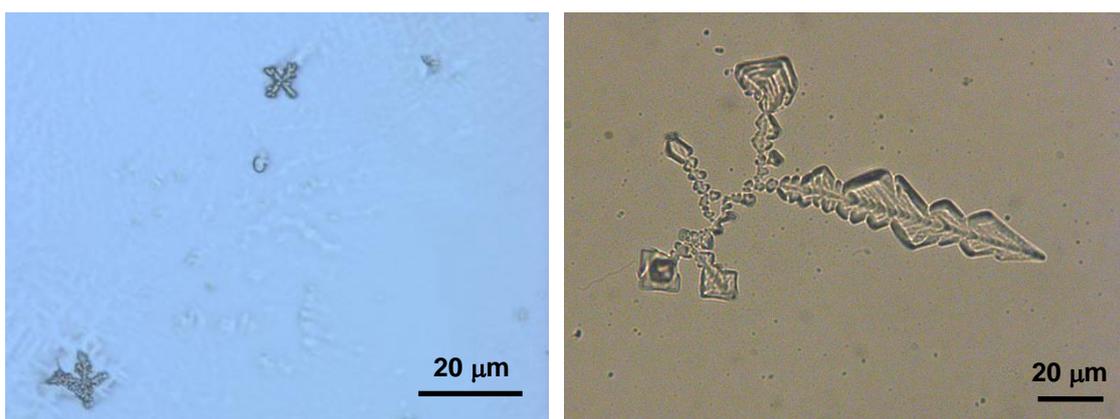


Figure S13. Optical microscopy images of aqueous dried samples of **5** (left) and **6** (right).

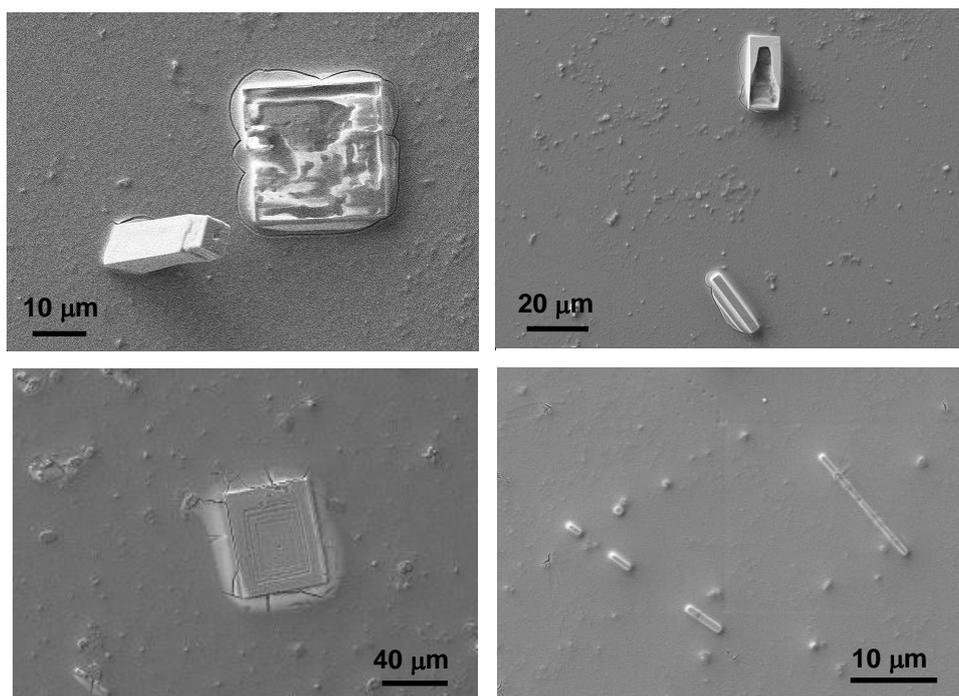


Figure S14. SEM images of aqueous dried samples of **5** (up) and **6** (bottom).

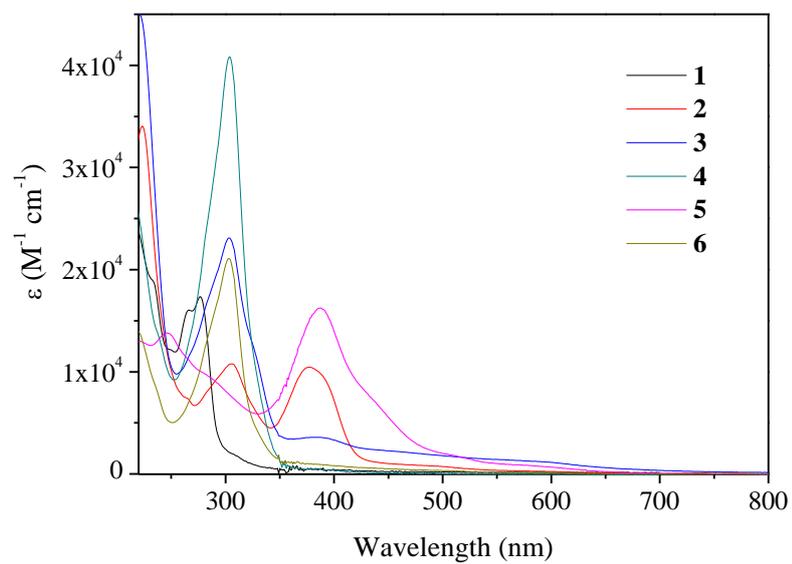


Figure S15. Absorption spectra of $5 \times 10^{-5} \text{M}$ solutions of complexes **1-6** in water.

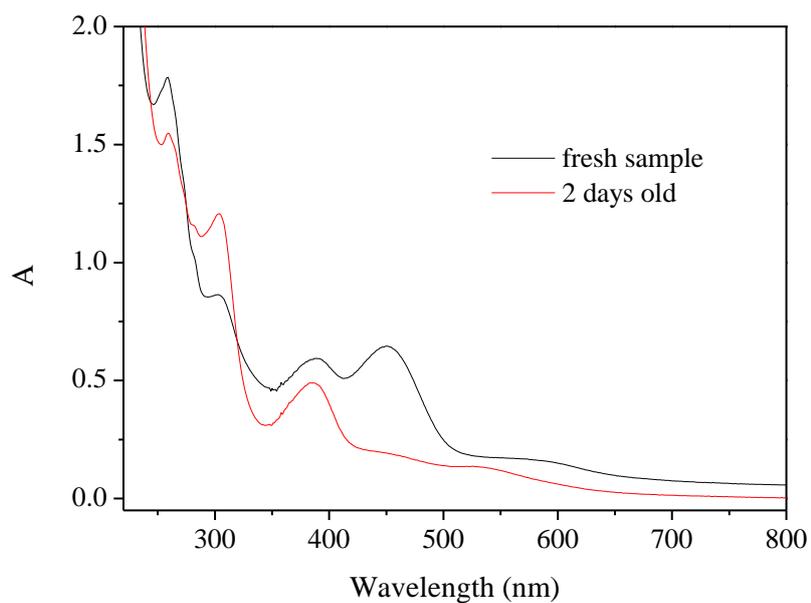


Figure S16. Absorption spectra of freshly prepared *ca.* 1×10^{-4} M solution (solid line) and after 2 days (red line) of **2** in water.

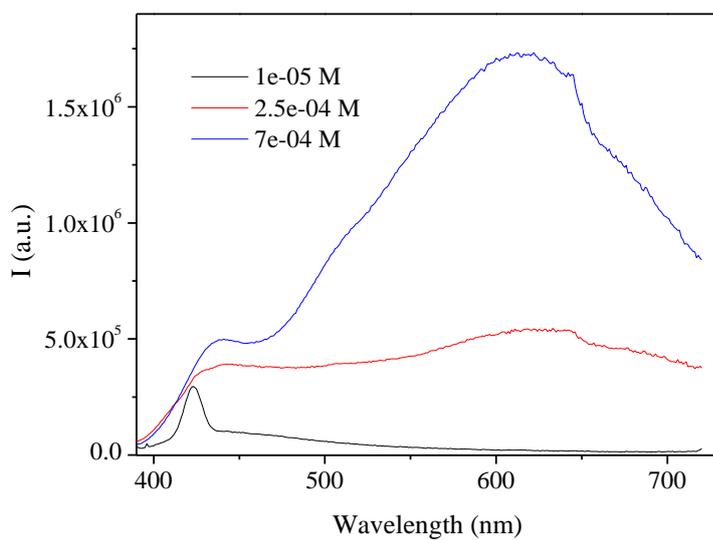


Figure S17. Emission spectra of **2** at three different concentrations in water. $\lambda_{\text{exc}} = 370$ nm.

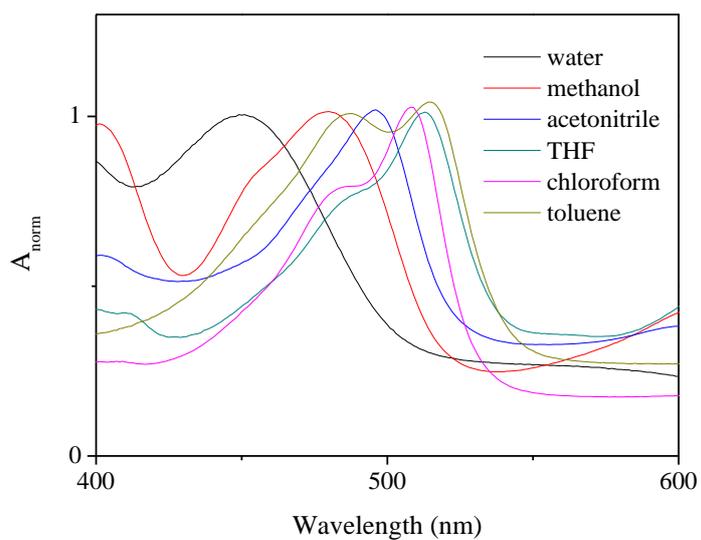


Figure S18. Hypsochromic effect with increasing polarity (negative solvatochromism) displayed in absorption spectra of complex 2. Absorption spectrum in cyclohexane was omitted due to the low solubility of the complex in this solvent.

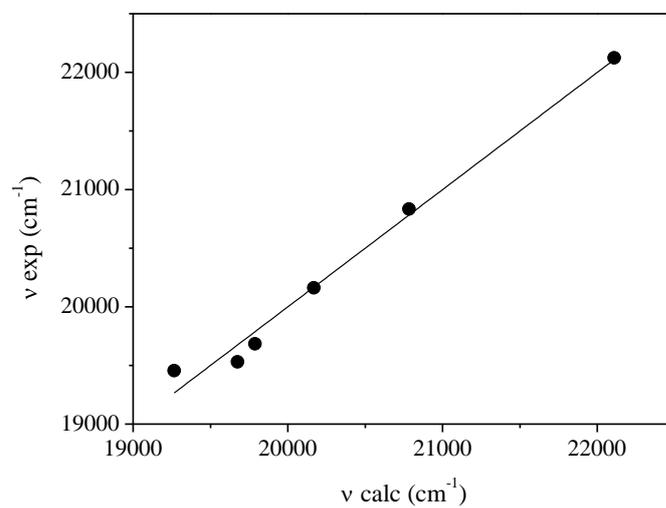


Figure S19. Plot of $\bar{\nu}_{\text{exp}}$ vs. $\bar{\nu}_{\text{calc}}$ for absorption data of compound 3.

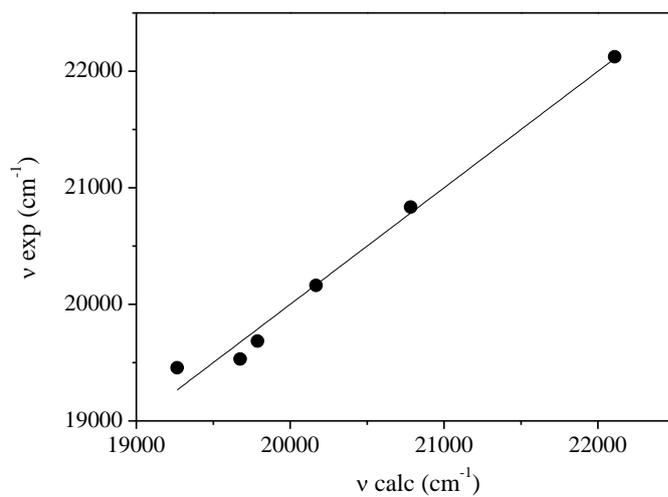


Figure S20. Plot of $\bar{\nu}_{0\text{exp}}$ vs. $\bar{\nu}_{0\text{calc}}$ for absorption data of compound **2**.

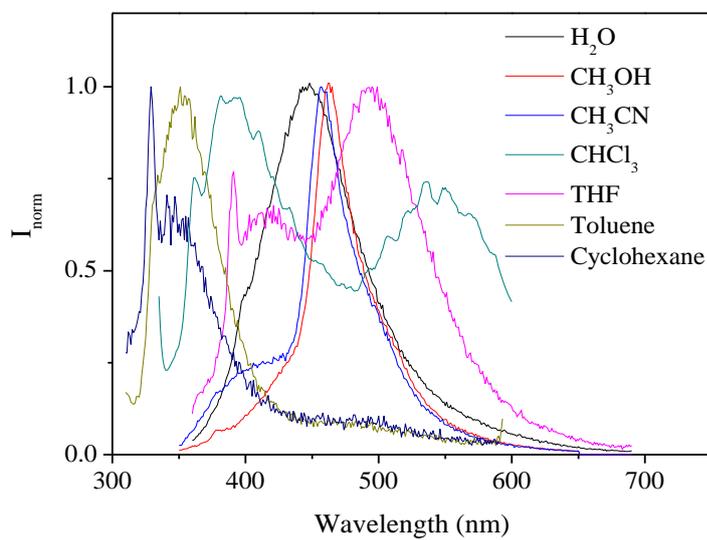


Figure S21. Normalized emission spectra of **3** in different solvents.

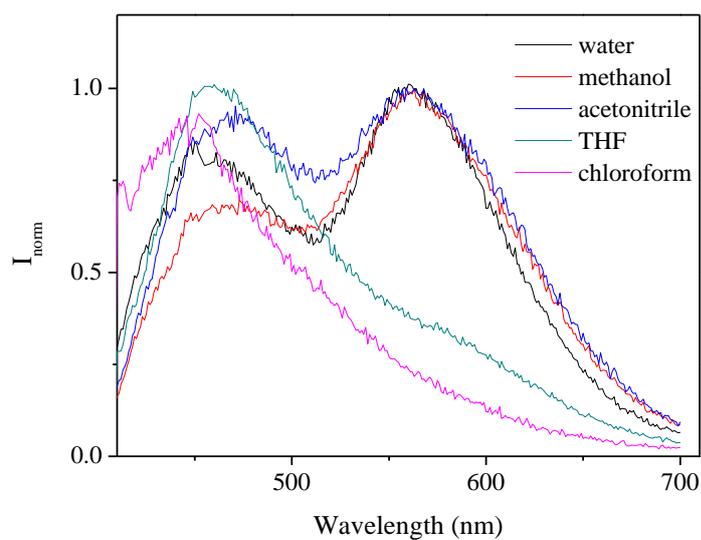


Figure S22. Normalized emission spectra of **5** in different solvents ($\lambda_{\text{exc}} = 370\text{nm}$). The complex is not emissive in the most apolar solvents toluene and cyclohexane.

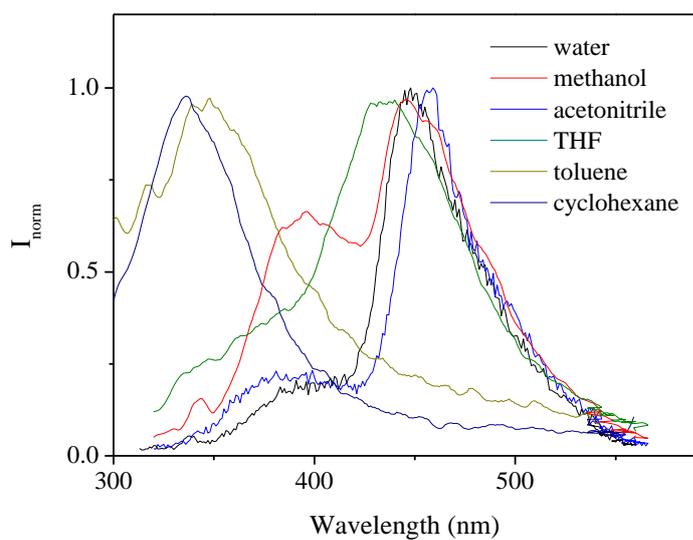


Figure S23. Normalized emission spectra of **6** in different solvents ($\lambda_{\text{exc}} = 300\text{nm}$). No significant emission was recorded in chloroform.

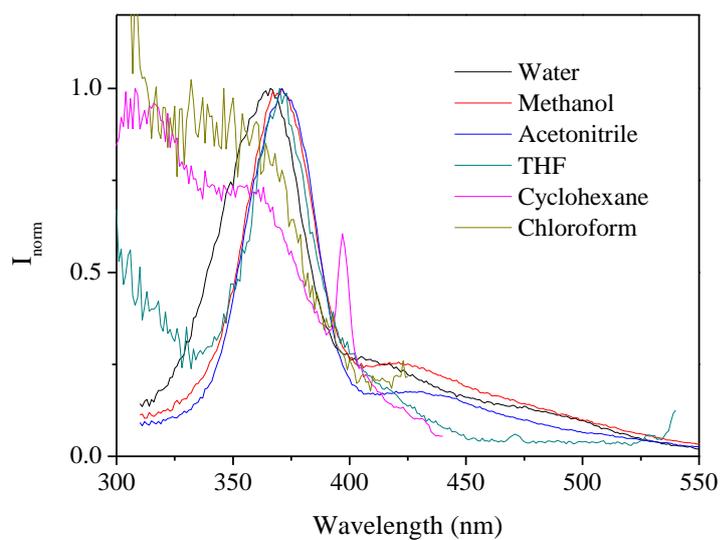


Figure S24. Normalized excitation spectra of **2** in different solvents.

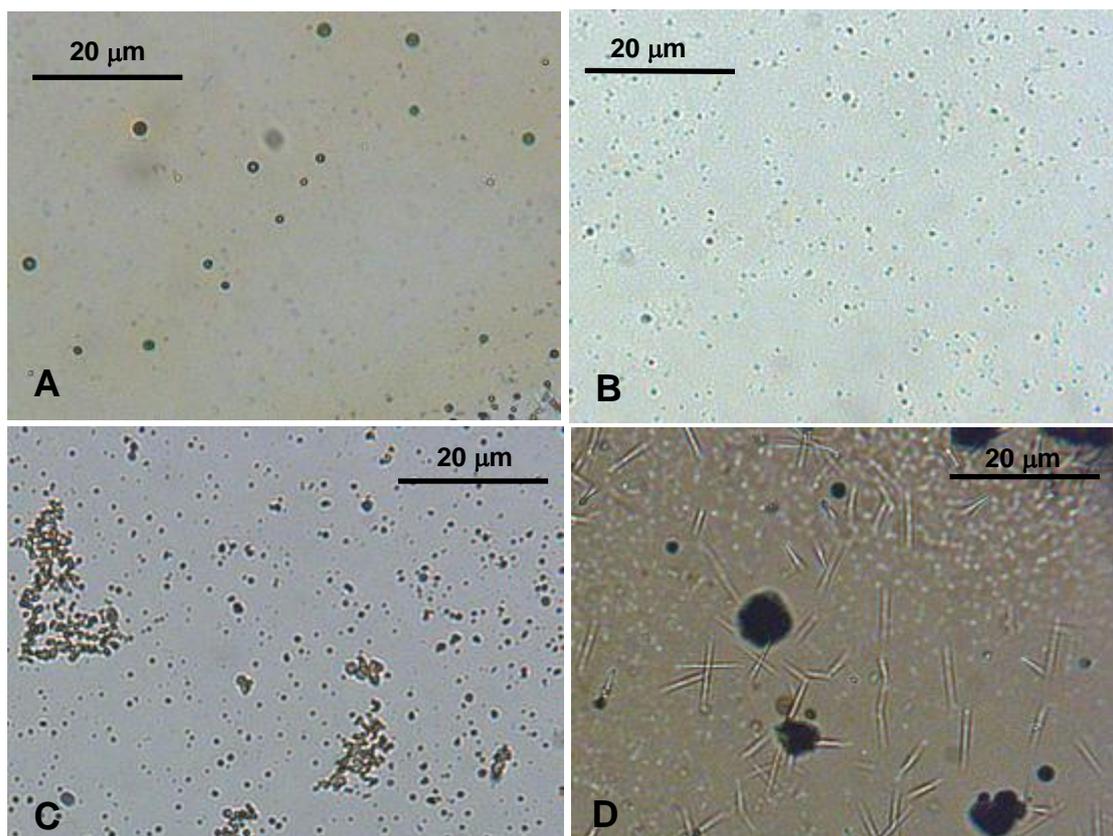


Figure S25. Optical microscopy images of **2** in water (A), methanol (B), acetonitrile (C) and CHCl_3 (D).

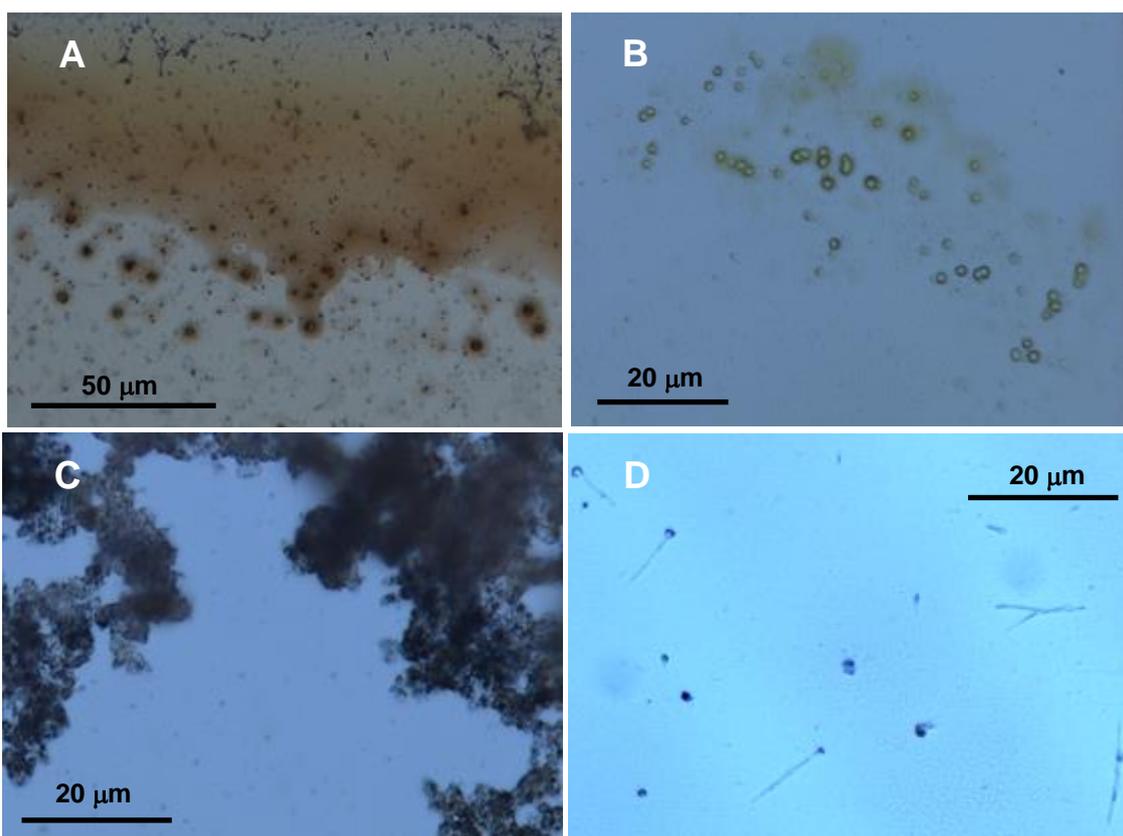


Figure S26. Optical microscopy images of **3** in water (A), methanol (B), acetonitrile (C) and CHCl₃ (D).

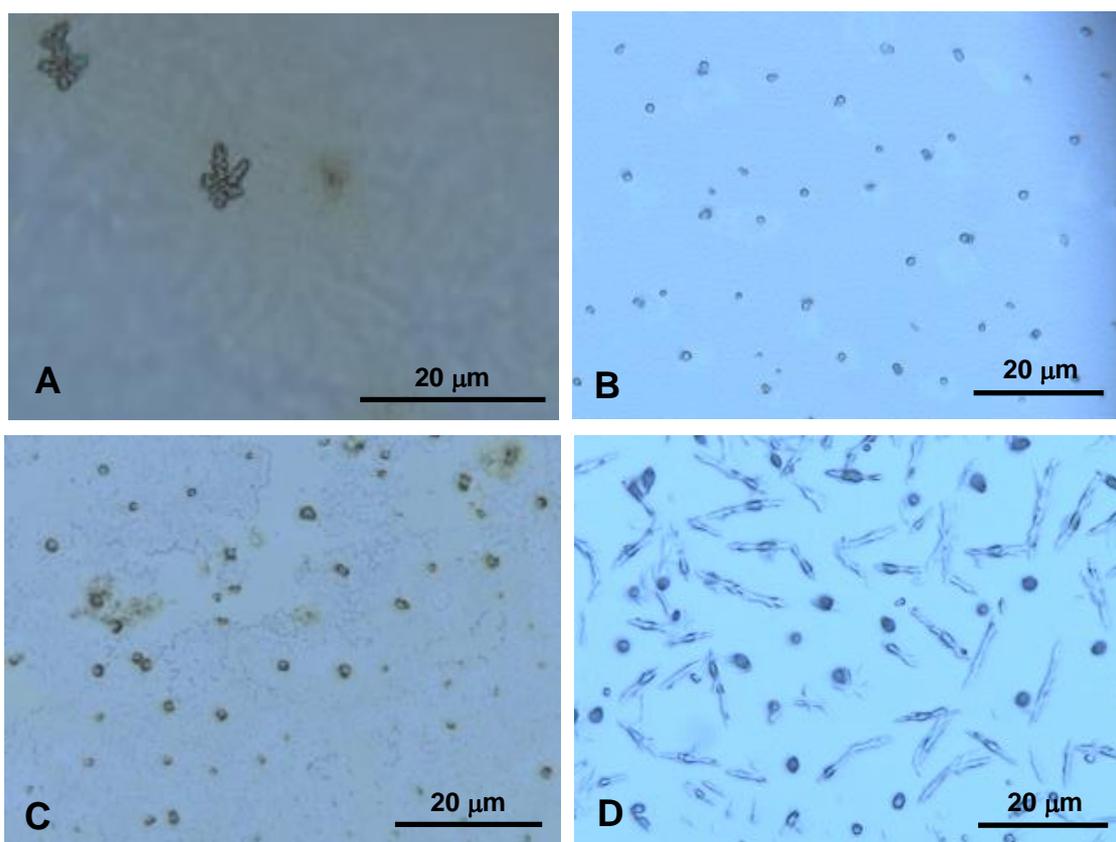


Figure S27. Optical microscopy images of **5** in water (A), methanol (B), acetonitrile (C) and CHCl₃ (D).

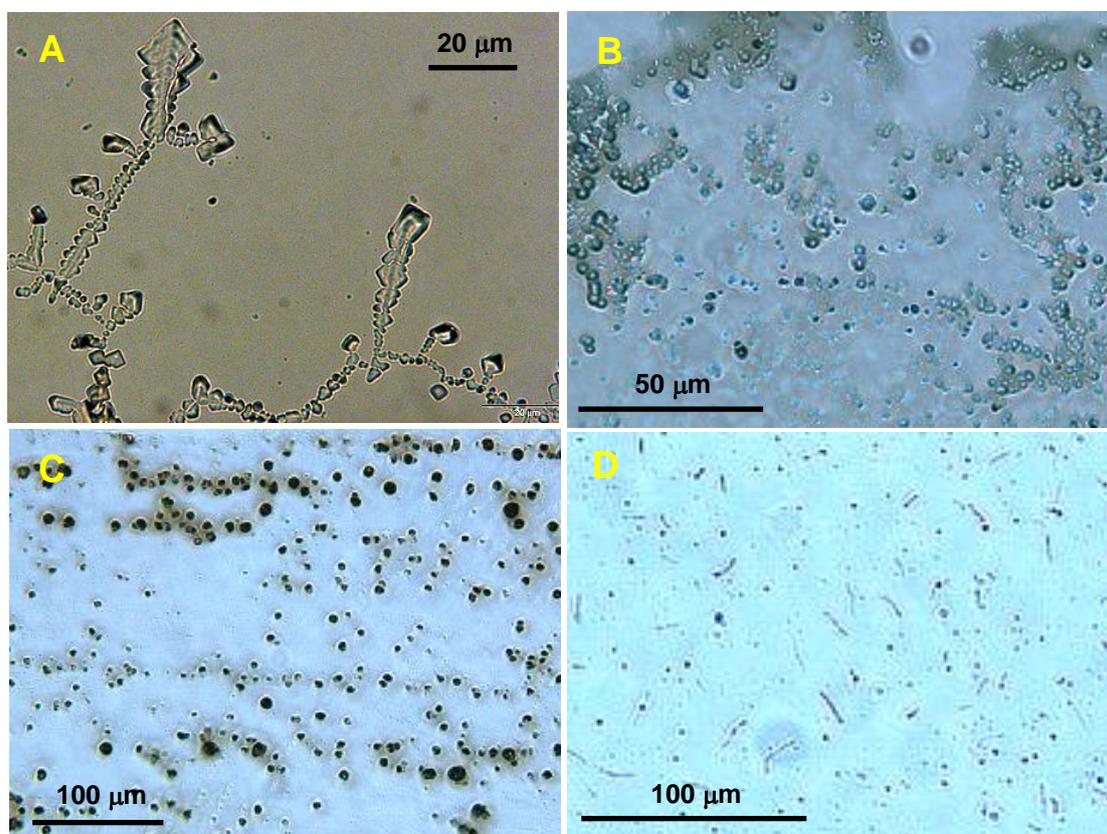
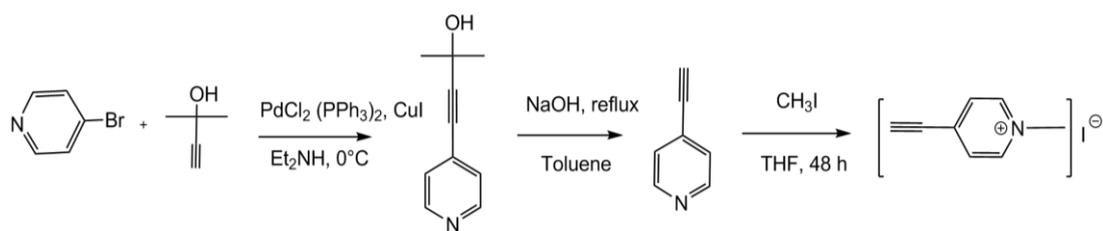
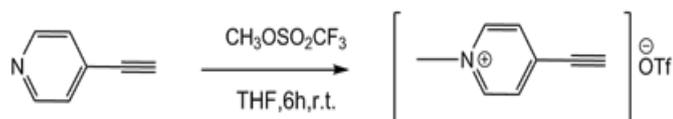


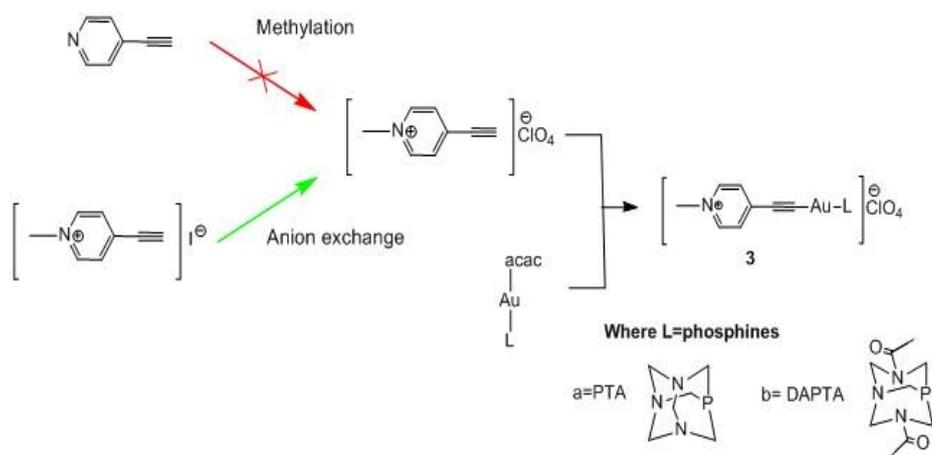
Figure S28. Optical microscopy images of **6** in water (A), methanol (B), acetonitrile (C) and CHCl₃ (D).



Scheme S1. Synthesis of N-methyl-4-ethynylpyridinium iodide.



Scheme S2. Synthesis of N-methyl-4-ethynylpyridinium triflate.



Scheme S3. Attempts for the synthesis of the N-methyl-4-ethynylpyridinium perchlorate derivatives. The syntheses were only successful by anion exchange procedure but in very low yields and not possible to isolate as solids.

Table S1. Absorption and emission ($\lambda_{\text{exc}} = 370$ nm) data of complexes **1-6** in water.* $\lambda_{\text{exc}} = 300$ nm

Compound	Absorption	Emission
	λ_{max} (nm) ($10^{-3} \epsilon$ ($\text{M}^{-1} \text{cm}^{-1}$))	(solution, λ_{max} (nm))
1	266 (16.0), 277 (17.4)	417, 438, 456, 550
2	302 (10.6), 380 (10.4)	430, 585
3	303 (23.1), 385 (3.6)	447
4	305 (40.8)	450*
5	243 (13.7), 387 (16.2)	455, 560
6	290 sh (15.9), 302 (21.0)	447

Table S2. α , β , π^* parameters for the solvents used.^a

Solvent	α	β	π^*	ϵ_r	n
Water	1.17	0.47	1.09	80.1	1.3330
Acetonitrile	0.19	0.31	0.75	35.94	1.3441
Methanol	0.93	0.62	0.60	32.66	1.3284
Tetrahydrofuran	0	0.55	0.55	7.58	1.4072
Chloroform	0.44	0	0.58	4.89	1.4459
Toluene	0	0.11	0.54	2.38	1.4969
Cyclohexane	0	0	0	2.02	1.4262

^a α : index of the solvent's ability to act as a hydrogen-bond donor (or electron pair acceptor) toward a solute; β : measure of the ability of a bulk solvent to act as a hydrogen-bond acceptor (or electron-pair donor); π^* : index of the solvent polarity/polarizability which measures the solvent's ability to stabilize a neighbouring charge or dipole through non-specific dielectric interactions; ϵ_r : solvent permittivity index; n: solvent refraction index.

Table S3. Absorption data of the XLCT band of **2** and **3** in different solvents.

Solvent	λ (2), nm (cm ⁻¹)	λ (3), nm (cm ⁻¹)
Water	452 (22124)	450 (22222)
Acetonitrile	496 (20161)	495 (20202)
Methanol	480 (20833)	487 (20534)
Tetrahydrofuran	508 (19685)	508 (19685)
Chloroform	512 (19531)	511 (19569)
Toluene	514 (19455)	515 (19417)