CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

Structures and Solvatochromic Phosphorescence of Dicationic Terpyridyl Platinum(II) Complexes with Foldable Oligo(*ortho*-phenyleneethynylene) Bridging Ligands

Ming-Xin Zhu, Wei Lu, Nianyong Zhu and Chi-Ming Che*[a]

[a] M. X. Zhu, Dr. W. Lu, Dr. N. Zhu, Prof. Dr. C. M. Che
Department of Chemistry and Open Laboratory of Chemical Biology of the Institute of Molecular Technology for Drug Discovery and Synthesis
The University of Hong Kong, Pokfulam Road, Hong Kong (China)

Ligand Synthesis:

H-(C≡C-1,2-C_6H_4)$_6$-C≡CH. A mixture of H-(C≡C-1,2-C_6H_4)$_4$-C≡CH (1.51g, 3.5mmol) and 2-I-C_6H_4-1-C≡C$Si(CH_3)_3$ (2.31 g, 7.7 mmol) were dissolved in 15 mL diethylamine (15 mL) and benzene (10 mL). After the solution was bubbled with argon for 30 min, $Pd(PPh_3)_2Cl_2$ (54 mg) and CuI (15 mg) were added, and the solution was stirred overnight. $(CH_3)_3Si$-(C≡C-1,2-C_6H_4)$_6$-C≡C$Si(CH_3)_3$ was obtained by chromatography on silica gel with hexane:CH_2Cl_2 (2:1) as eluent, and was desilylated with excess KOH in CH_3OH/THF solution. Yield: 1.68 g, 77%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.62–7.52 (m, 10H), 7.48–7.46 (m, 2H), 7.29–7.20 (m, 12H), 3.22 ppm (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ = 132.6, 132.5, 132.41, 132.38, 132.35, 128.6, 128.3, 128.14, 128.11, 128.08, 128.07, 126.5, 125.93, 125.86, 125.6, 124.6, 92.6, 92.5, 92.0, 82.3 and 81.5 ppm; EI-MS: *m*/*z*: 624 $[M-2]^+$.

H-(C≡C-1,2-C_6H_4)$_8$-C≡CH. A mixture of H-(C≡C-1,2-C_6H_4)$_6$-C≡CH (1.30 g, 2.1 mmol) and 2-I-C_6H_4-1-C≡C$Si(CH_3)_3$ (1.25 g, 4.2 mmol) were dissolved in diethylamine (15 mL) and benzene (10 mL). After the solution was bubbled with argon for 30 min, $Pd(PPh_3)_2Cl_2$ (30 mg) and CuI (8 mg) were added, and the solution was stirred overnight. $(CH_3)_3Si$-(C≡C-1,2-C_6H_4)$_8$-C≡C$Si(CH_3)_3$ was obtained by chromatography on silica gel with hexane:CH_2Cl_2 (2:1) as eluent, and was desilylated with excess KOH in CH_3OH/THF solution. Yield: 1.30 g, 75%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ (ppm) = 7.56–7.52 (m, 16H), 7.25–7.22 (m, 16H), 3.22 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 ^{o}C): δ (ppm) = 132.6, 132.5, 132.43, 132.39, 132.34, 132.28 128.6, 128.3, 128.2, 128.12, 128.08, 126.5, 126.0, 125.8, 125.7, 125.6, 124.6, 92.7, 92.6, 92.5, 92.0, 82.3 and 81.5 ppm; FAB-MS (+ve): *m*/*z*: 827 $[M+1]^+$.

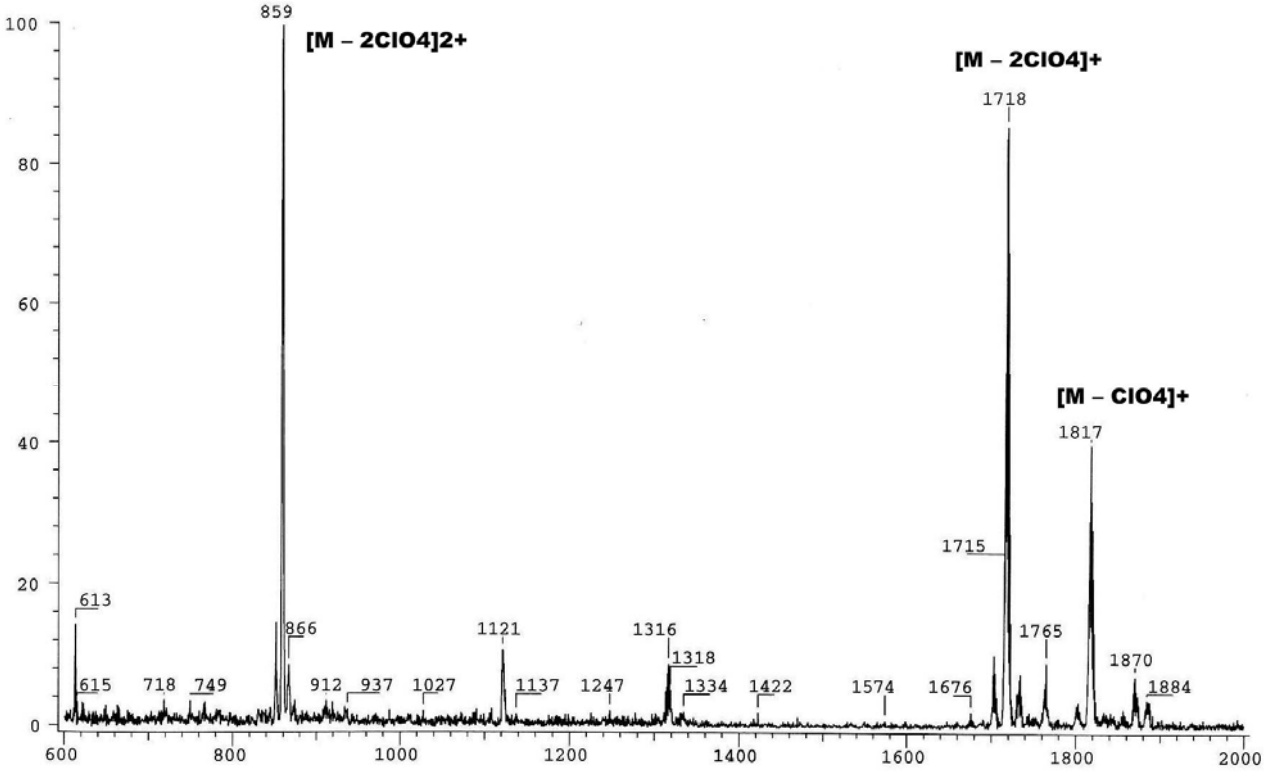

Figure S1 FAB mass spectrum of **5**.

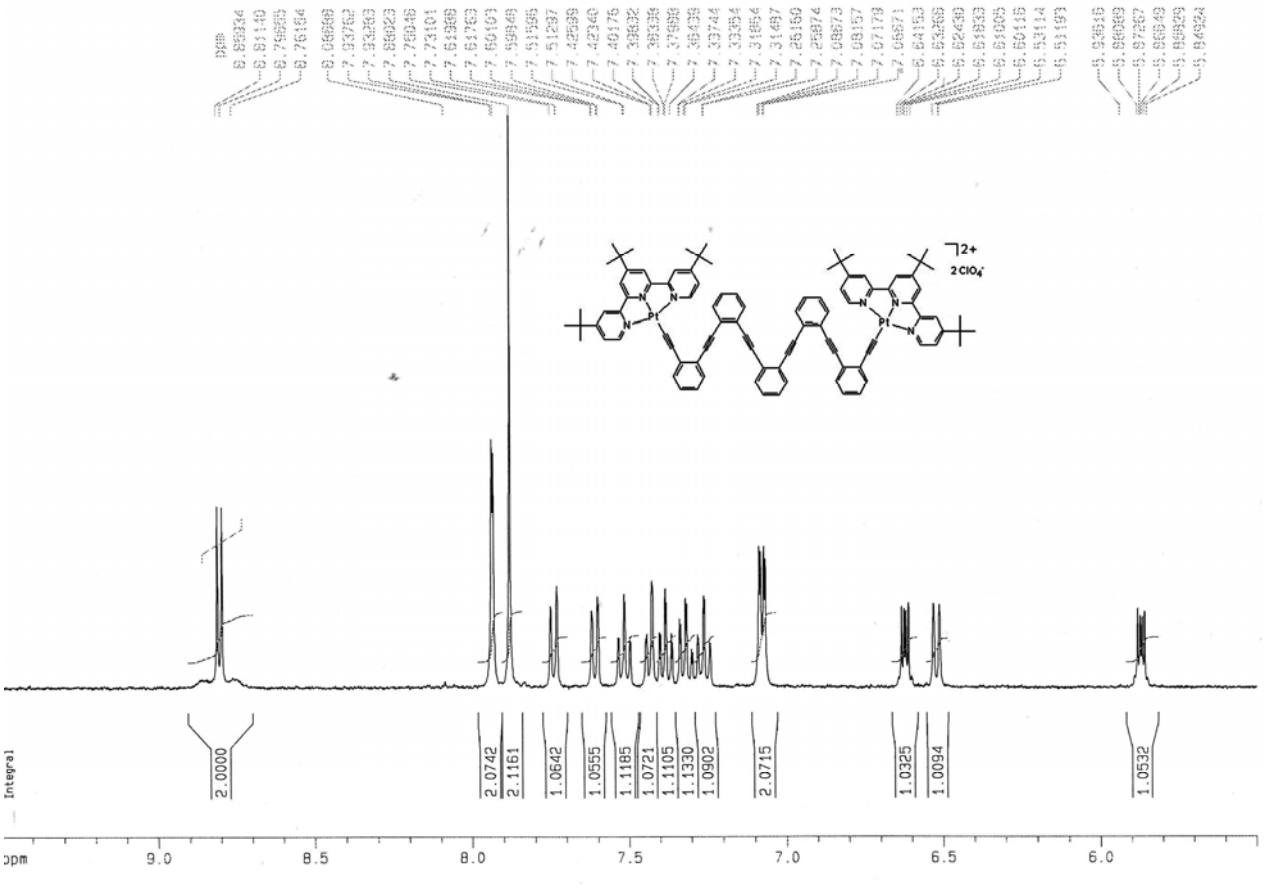

Figure S2 ^{1}H NMR spectra of **5** at the aromatic region in CD_3CN solution.

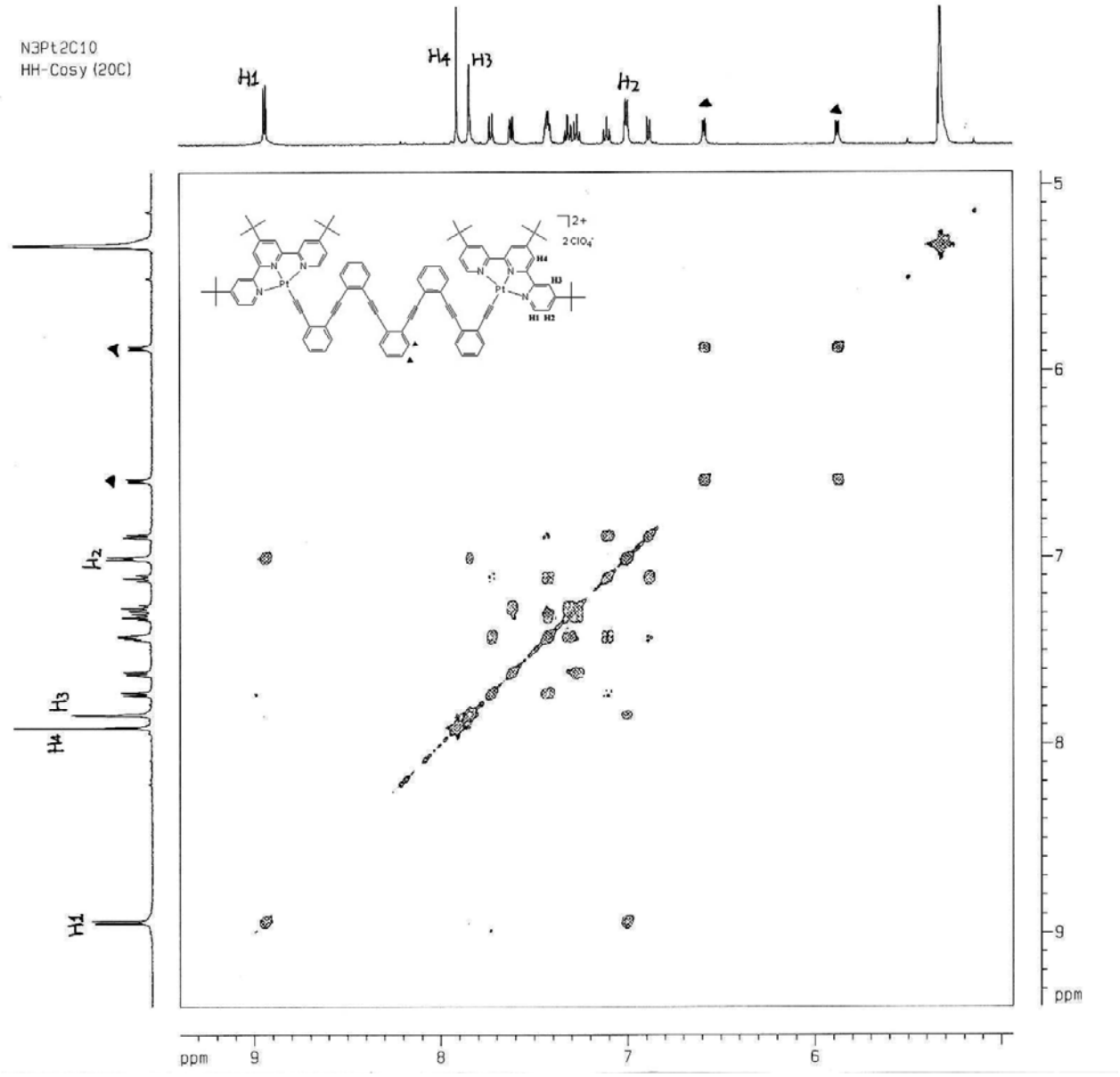

Figure S3 ^{1}H-^{1}H COSY NMR spectrum of **5** in CD_2Cl_2 solution (~ 5×10^{-3} M) at 20 ^{o}C.

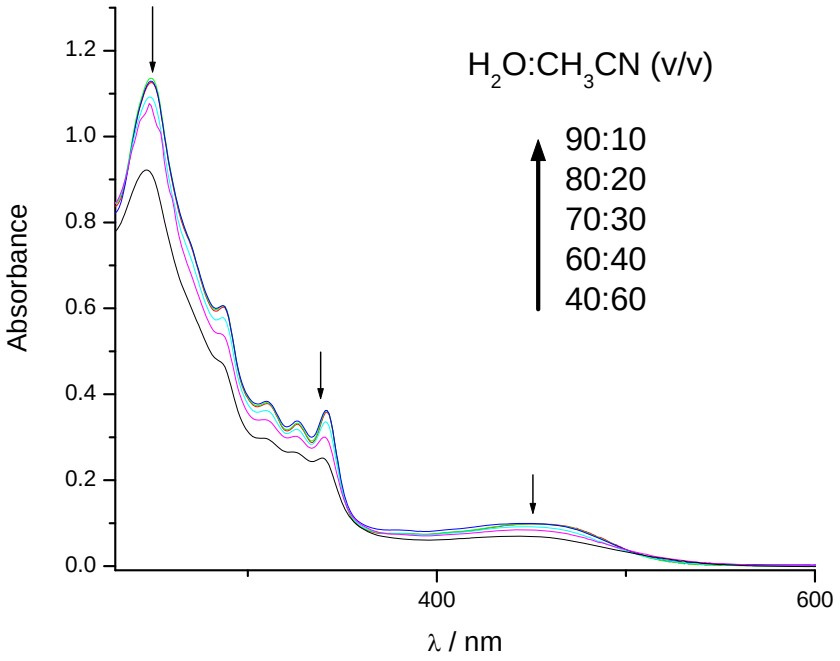

Figure S4 UV-vis absorption traces of **1** in H_2O/CH_3CN mixtures upon increasing the water fraction.

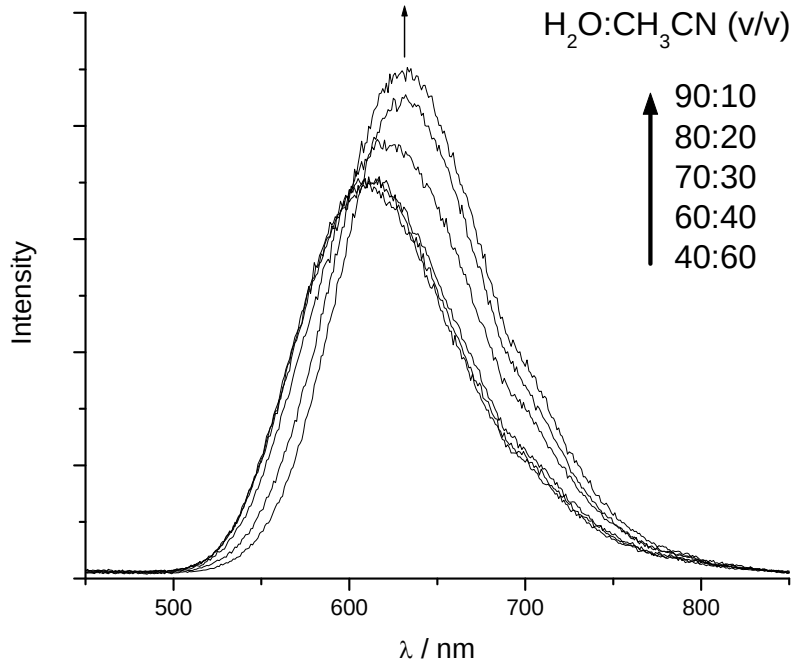

Figure S5 Emission traces of **1** in H_2O/CH_3CN mixtures upon increasing the water fraction.

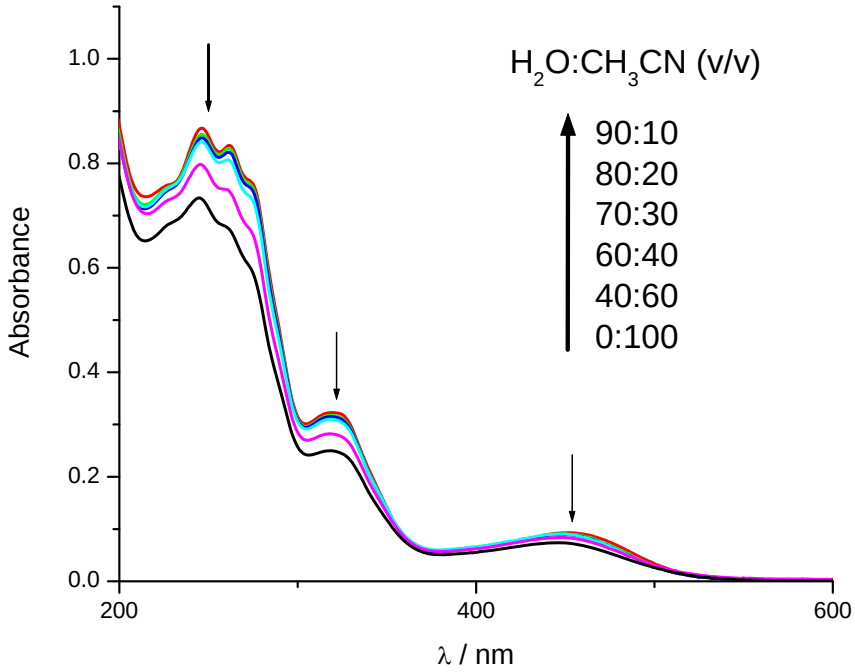

Figure S6 UV-vis absorption traces of **2** in H_2O/CH_3CN mixtures upon increasing the water fraction.

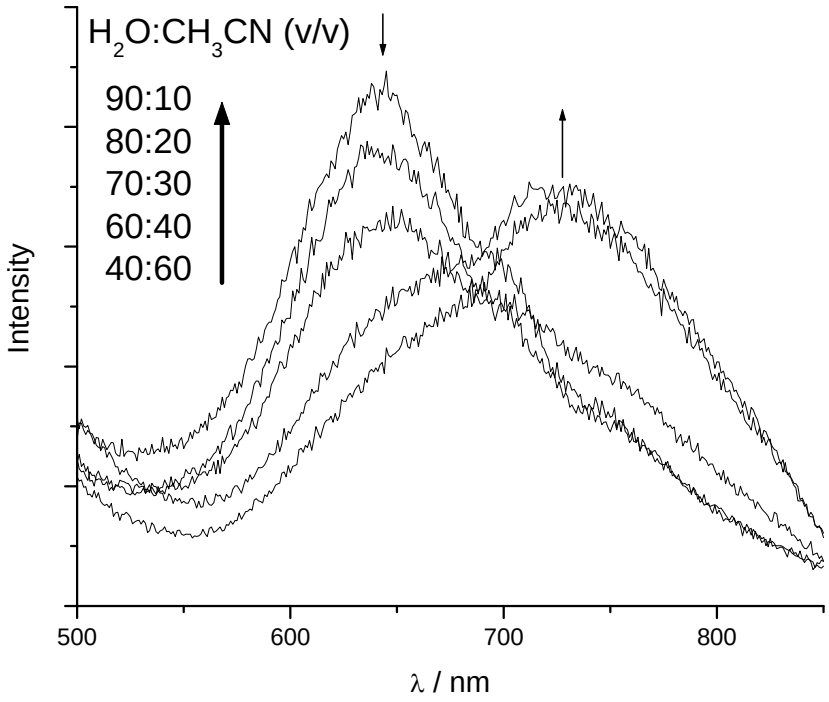

Figure S7 Emission traces of **2** in H_2O/CH_3CN mixtures upon increasing the water fraction.

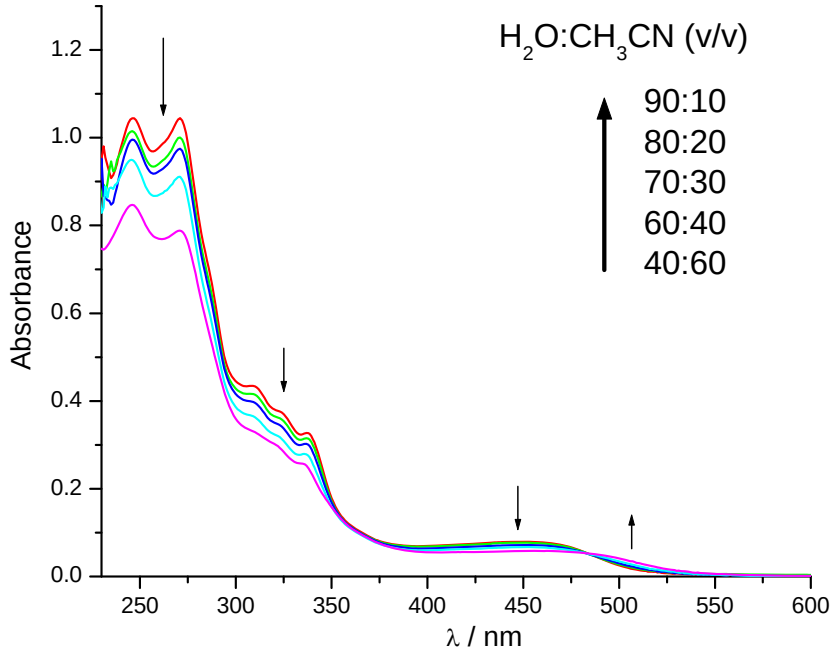

Figure S8 UV-vis absorption traces of **3** in H_2O/CH_3CN mixtures upon increasing the water fraction.

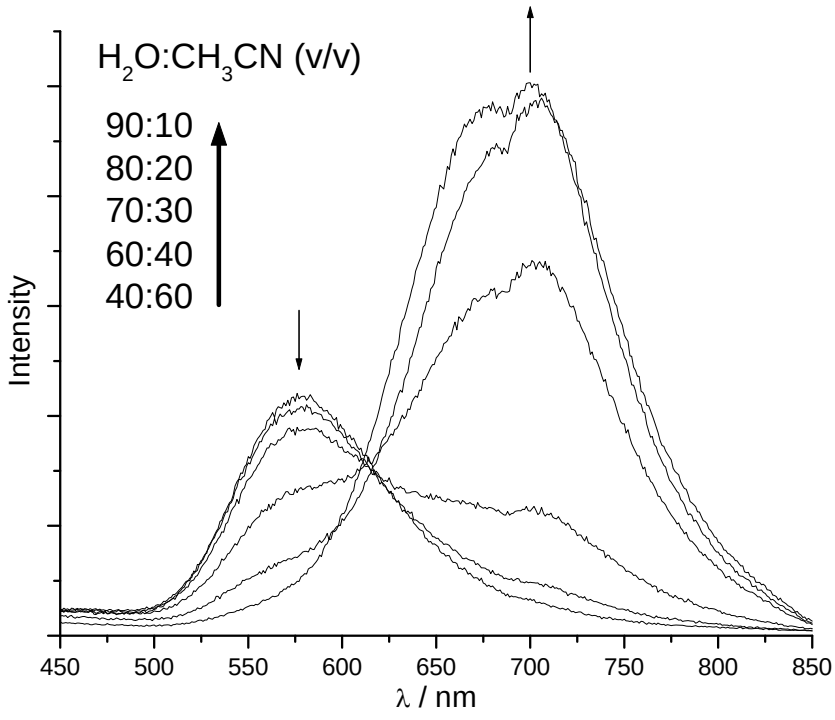

Figure S9 Emission traces of **3** in H_2O/CH_3CN mixtures upon increasing the water fraction.

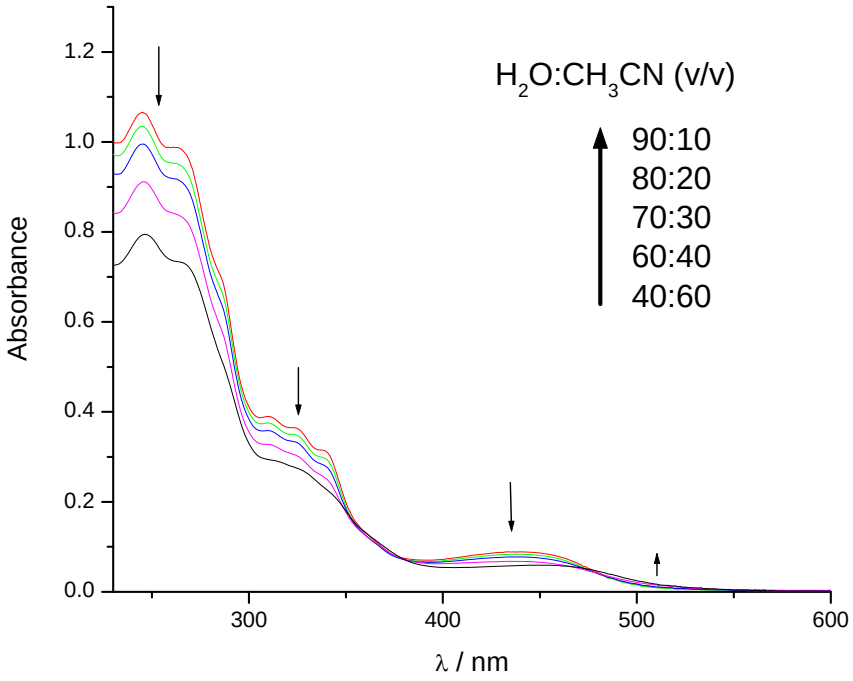

Figure S10 UV-vis absorption traces of **4** in H_2O/CH_3CN mixtures upon increasing the water fraction.

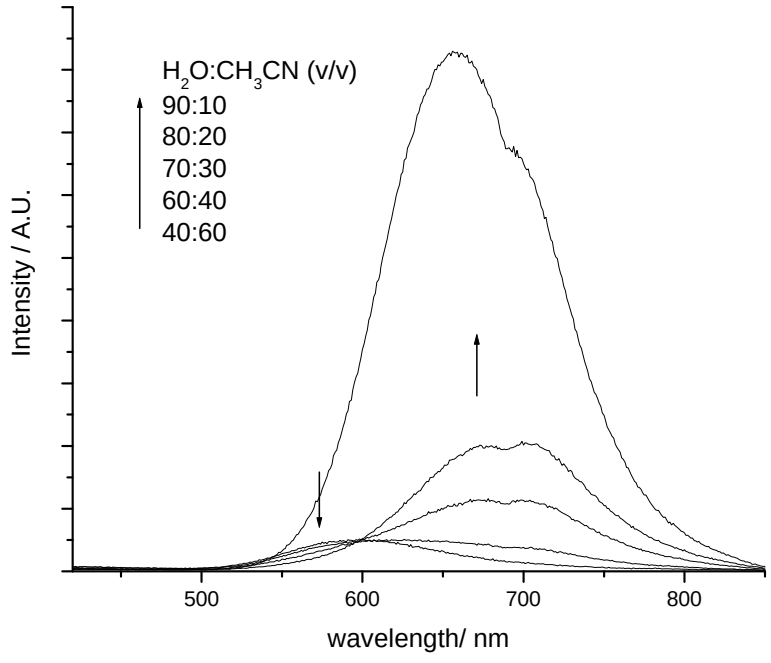

Figure S11 Emission traces of **4** in H_2O/CH_3CN mixtures upon increasing the water fraction.

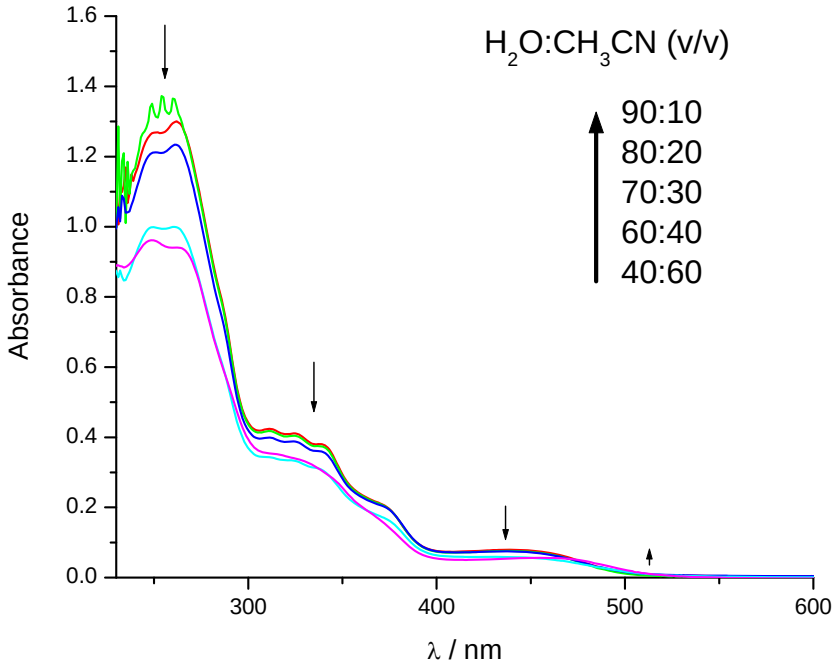

Figure S12 UV-vis absorption traces of **6** in H_2O/CH_3CN mixtures upon increasing the water fraction.

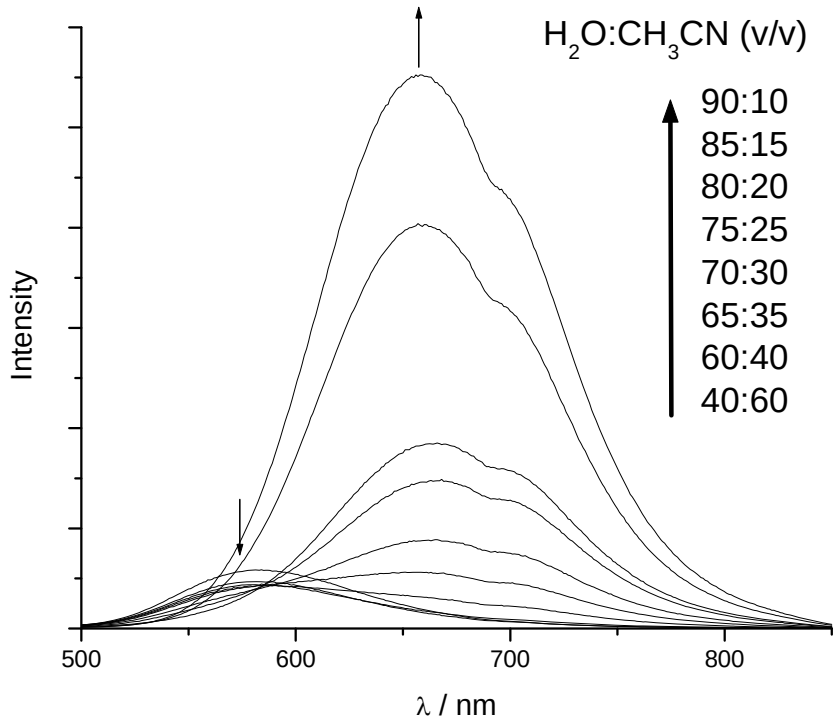

Figure S13 Emission traces of **6** in H_2O/CH_3CN mixtures upon increasing the water fraction.

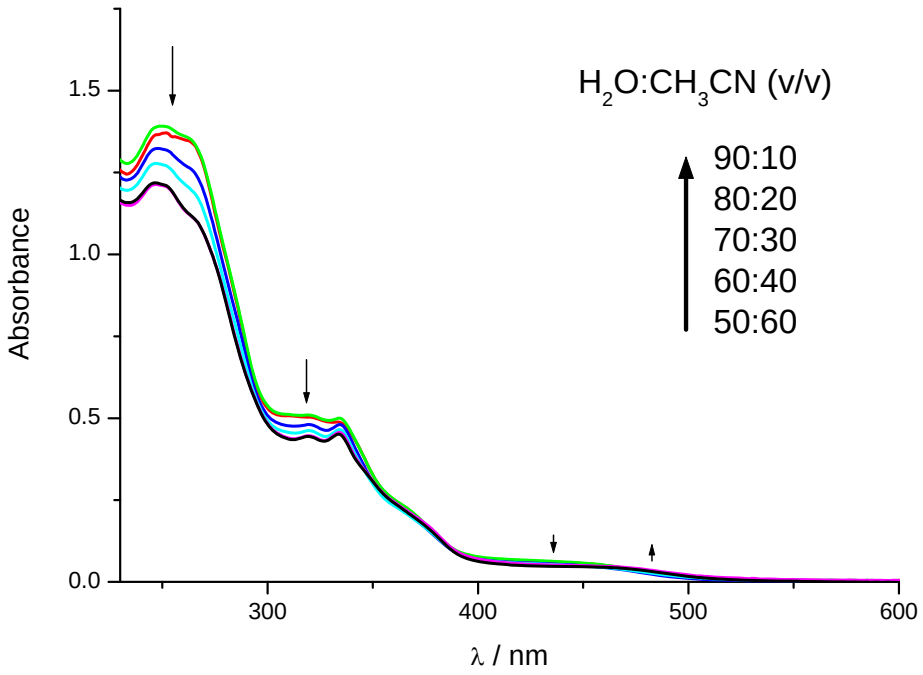

Figure S14 UV-vis absorption traces of **7** in H_2O/CH_3CN mixtures upon increasing the water fraction.

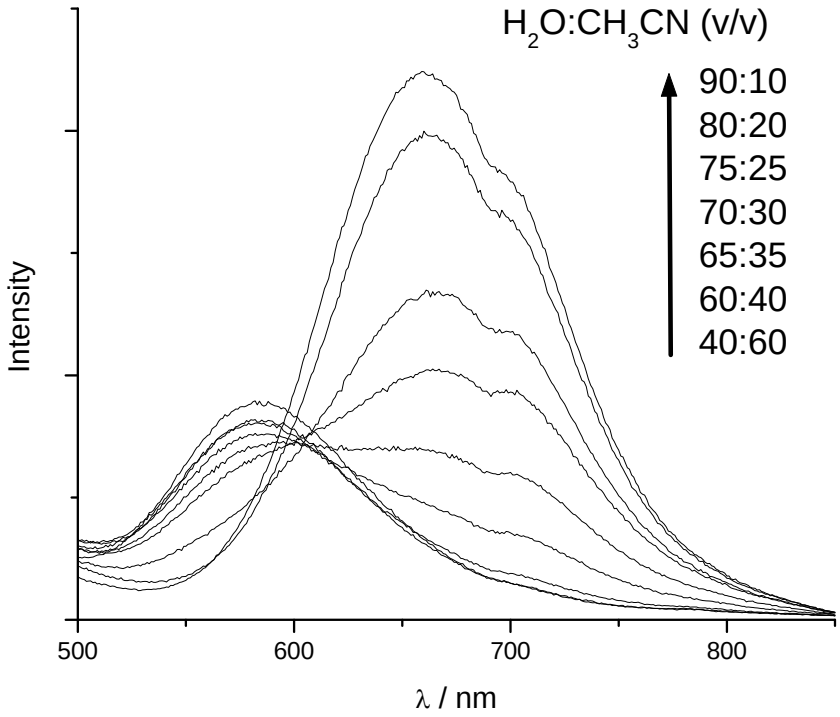

Figure S15 Emission traces of **7** in H_2O/CH_3CN mixtures upon increasing the water fraction.

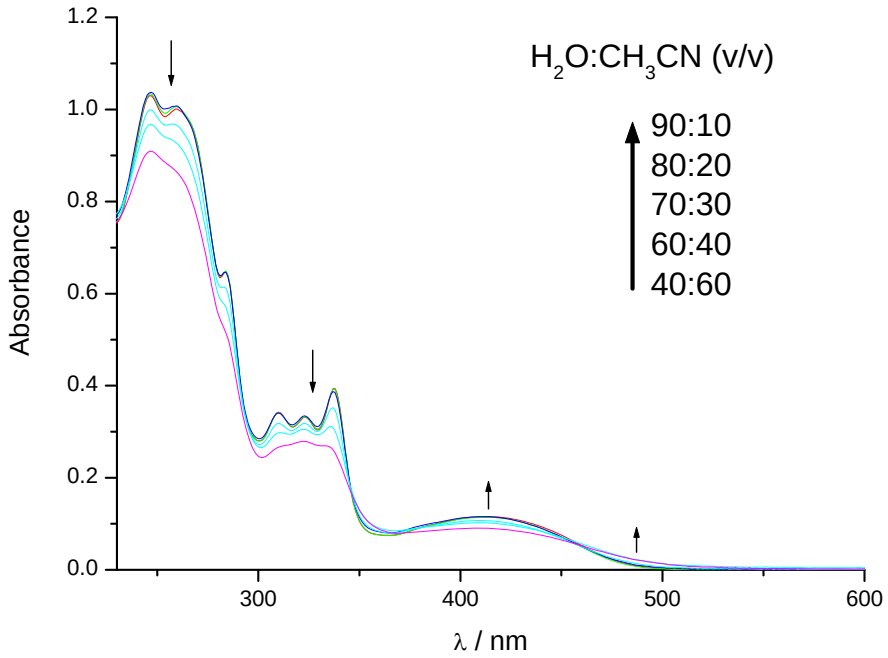

Figure S16 UV-vis absorption traces of **8** in H_2O/CH_3CN mixtures upon increasing the water fraction.

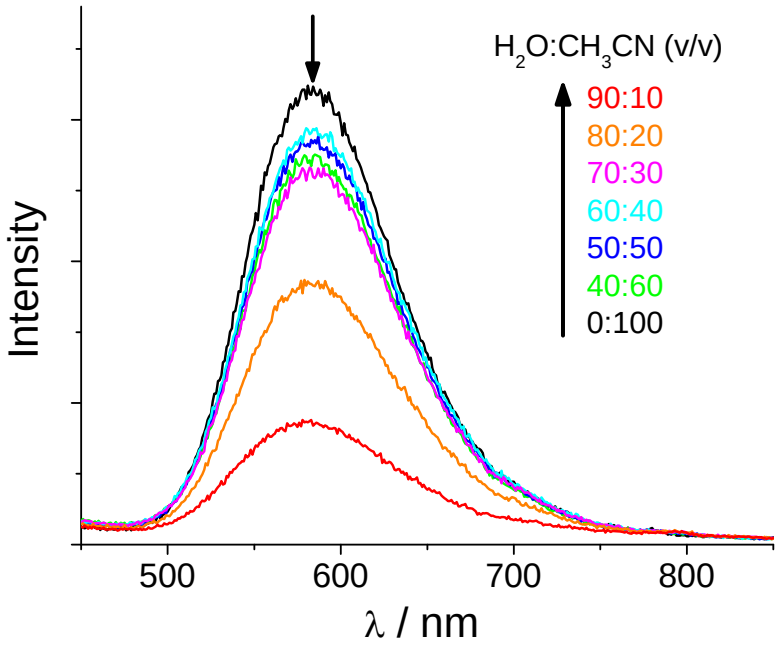

Figure S17 Emission traces of **8** in H_2O/CH_3CN mixtures upon increasing the water fraction.

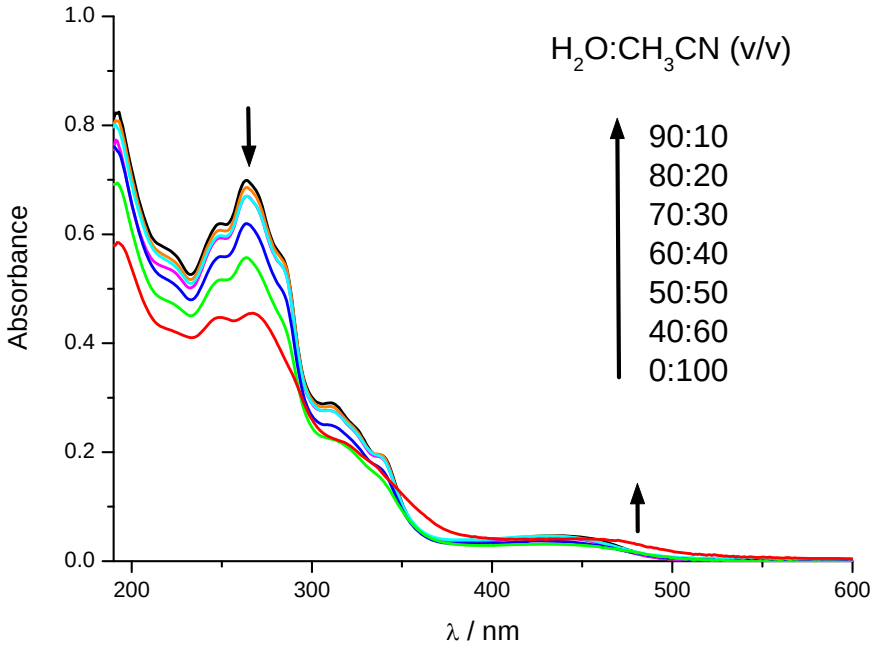

Figure S18 UV-vis absorption traces of **9** in H_2O/CH_3CN mixtures upon increasing the water fraction.

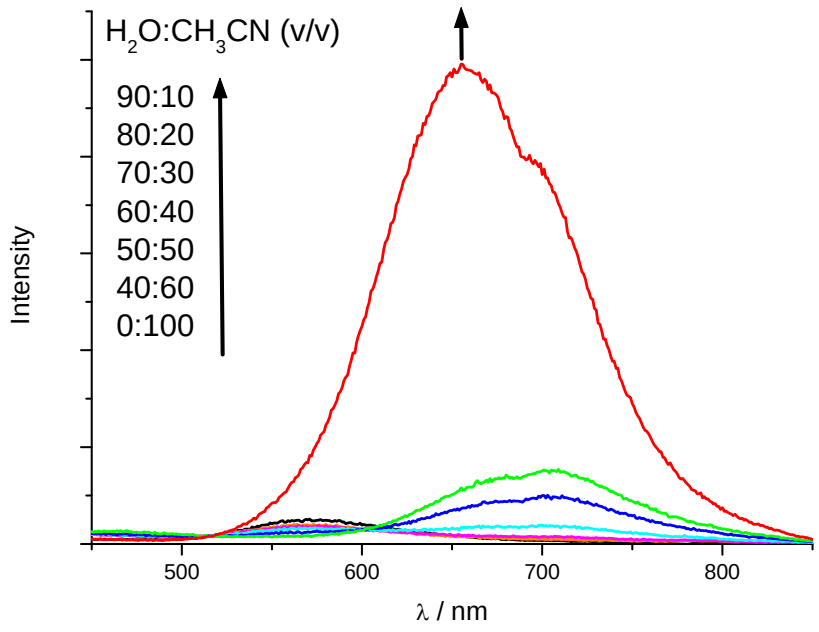

Figure S19 Emission traces of **9** in H_2O/CH_3CN mixtures upon increasing the water fraction.

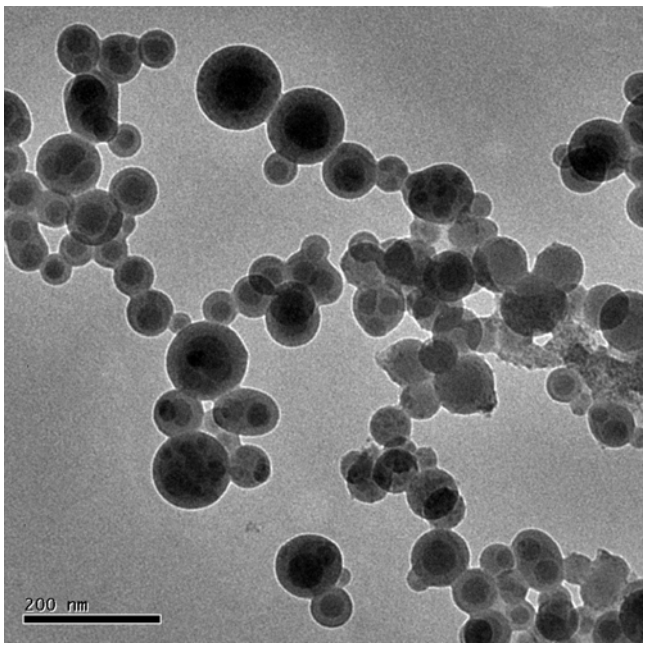

Figure S20 TEM image of **8** in H_2O/CH_3CN mixtures at 90% water fraction showing spherical nanoparticles.

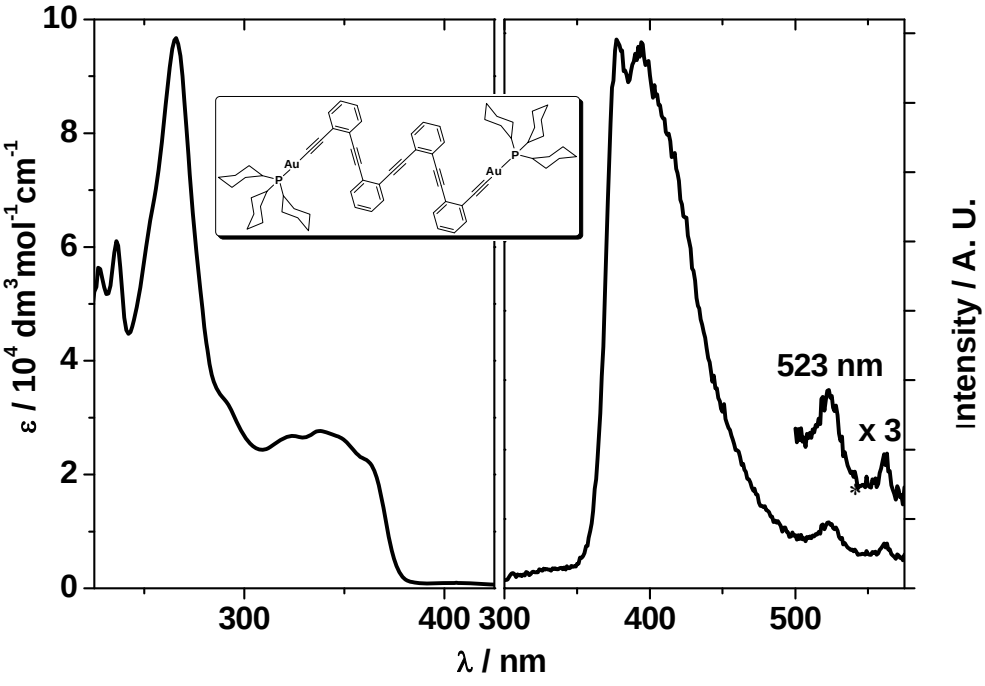

Figure S21 Absorption and emission spectra of complex $[(Cy_3P)Au\text{-}C{\equiv}C\text{-}1,2\text{-}C_6H_4\text{-}(C{\equiv}C\text{-}1,2\text{-}C_6H_4)_3\text{-}C{\equiv}C\text{-}Au(Cy_3P)]$ (Cy = cyclohexyl, as shown in the inset) in degassed CH_2Cl_2 solution at 298 K showed a weak 0-0 phosphorescence band at λ_{max} at 523 nm.