Electronic Supporting Information

Structure and Luminescence Properties of a Well-Known Macrometallocyclic Trinuclear Au(I) Complex and Its Adduct with a Perfluorinated Fluorophore Showing Cooperative Anisotropic Supramolecular Interactions

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1. Synthetic Details

All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Solvents were purchased from commercial sources, distilled from conventional drying agents and degassed by the freeze-pump-thaw method prior to use. Octafluoronaphthalene ($C_{10}F_8$) was obtained from Matrix Scientific and was used as received (96 %). Synthesis of [Au(μ-C^2,N^3-bzim)]$_3$ (**1**) was performed according to a published procedure.[1] Crystals of **1** were grown by slow evaporation from hexane/dichloromethane solution. The adduct **1**•$C_{10}F_8$ was synthesized by dissolving 50 mg (0.045 mmol) of **1** in 5 mL of dichloromethane and adding to it a 12.5 mg (0.045 mmol) of octafluoronaphthalene in 5 mL hexane . The solution is stirred for one hour. Colorless single crystals used in the crystallographic and luminescence studies were grown by slow evaporation for several days from a THF solution. Yield (45 mg, 80 %). M.p. 190 º C (vs. 89-90º C for octafluoronaphthalene and 240º C for **1**).

2. Photophysical Measurements

Steady-state luminescence spectra were acquired with a PTI QuantaMaster Model QM-4 scanning spectrofluorometer equipped with a 75-watt xenon lamp, emission and excitation monochromators, excitation correction unit, and a PMT detector. The emission spectra were corrected for the detector wavelength dependent response. The excitation spectra were also corrected for the wavelength dependent lamp intensity, but the correction was done only at $\lambda >$ 240 nm due to the unreliability of the correction at shorter wavelengths at which the samples here absorb and the xenon lamp output is rather low. Long-pass filters were used to exclude light scattering due to the excitation source from reaching the detector. Temperature-dependent

studies were acquired with an Oxford optical cryostat using liquid helium as a coolant. Lifetime data were acquired using a nitrogen laser interfaced with a tunable dye laser and a frequency doubler, as part of fluorescence and phosphorescence sub-system add-ons to the PTI instrument. The 337.1 nm line of the N_2 laser was used to pump a freshly-prepared 1×10^{-2} M solution of the organic continuum laser dye Coumarin-540A in ethanol, the output of which was tuned and frequency doubled to attain the 290 nm excitation. Luminescence and lifetime studies for frozen solutions were conducted for selected samples by placing a 5 mm Suprasil quartz cylindrical tube containing the appropriate solution in a liquid nitrogen filled Dewar flask with a Suprasil quartz cold finger and then inserting this setup in the sample compartment of the PTI instrument.

The fluorescence luminescence spectra were acquired with a PTI spectrofluorometer described above. For titration experiments, 3.00 mL of a 2.18 x 10^{-4} M solution of F_8-naphthalene in CH_2Cl_2 was added into a quartz cuvette, and the sample was excited at λ_{exc} = 290 nm and its fluorescence spectrum measured. At each titration data point, an increment of 20, 60, 100, 200, 300, 400, and 600 μL of 0.007 M solution of compound **1** in CH_2Cl_2 was added to the cuvette, and the emission intensity at λ_{max} = 350 nm was measured within 1 minute of the addition. The intensity data were fit to the Stern-Volmer equation:

$$I_o/I = 1 + K_{sv}[Q]$$

(where I_o and I are the fluorescence intensities without and with quencher, respectively, K_{SV} is the Stern-Volmer constant, and [Q] is the concentration of quencher added). The initial intensity divided by the intensity upon addition of **1** was plotted versus the concentration of **1** added. A linear least square fit of the data points afforded the K_{SV}.

3. X-ray Crystallographic Details

Crystal structure determination for compounds **1** and **1**•$C_{10}F_8$ were carried out using a Bruker SMART APEX2 CCD-based X-ray diffractometer equipped with a low Oxford Cryosystems temperature device and Mo-target X-ray tube (wavelength = 0.71073 Å). Measurements were taken at 296(2) and 100(2) K for crystals of **1** and **1**•$C_{10}F_8$, respectively. Data collection, indexing, and initial cell refinements were carried out using APEX2,[2] frame integration and final cell refinements were done using SAINT.[3] An absorption correction was applied using the program SADABS.[4] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in the compounds **1** and **1**•$C_{10}F_8$ were placed in idealized positions and were refined as riding atoms. Structure solution, refinement, graphic and generation of publication materials were performed by using SHELXTL software.[5] Refinement details and structural parameters for the compounds **1** and **1**•$C_{10}F_8$ are summarized in Tables S1 and S2.

4. Supplementary Figures

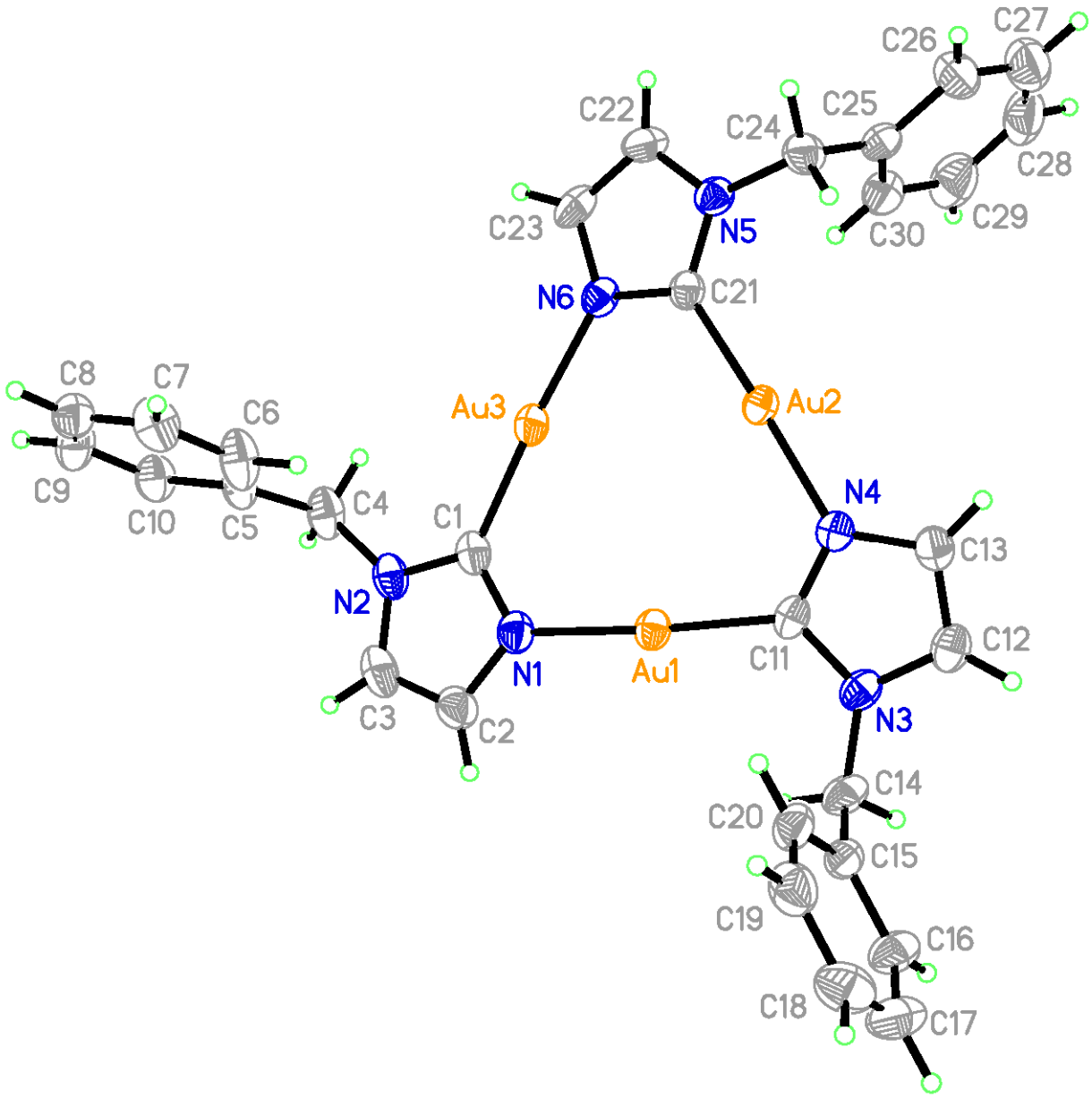

Fig. S1 ORTEP view of the molecular structure of **1**.

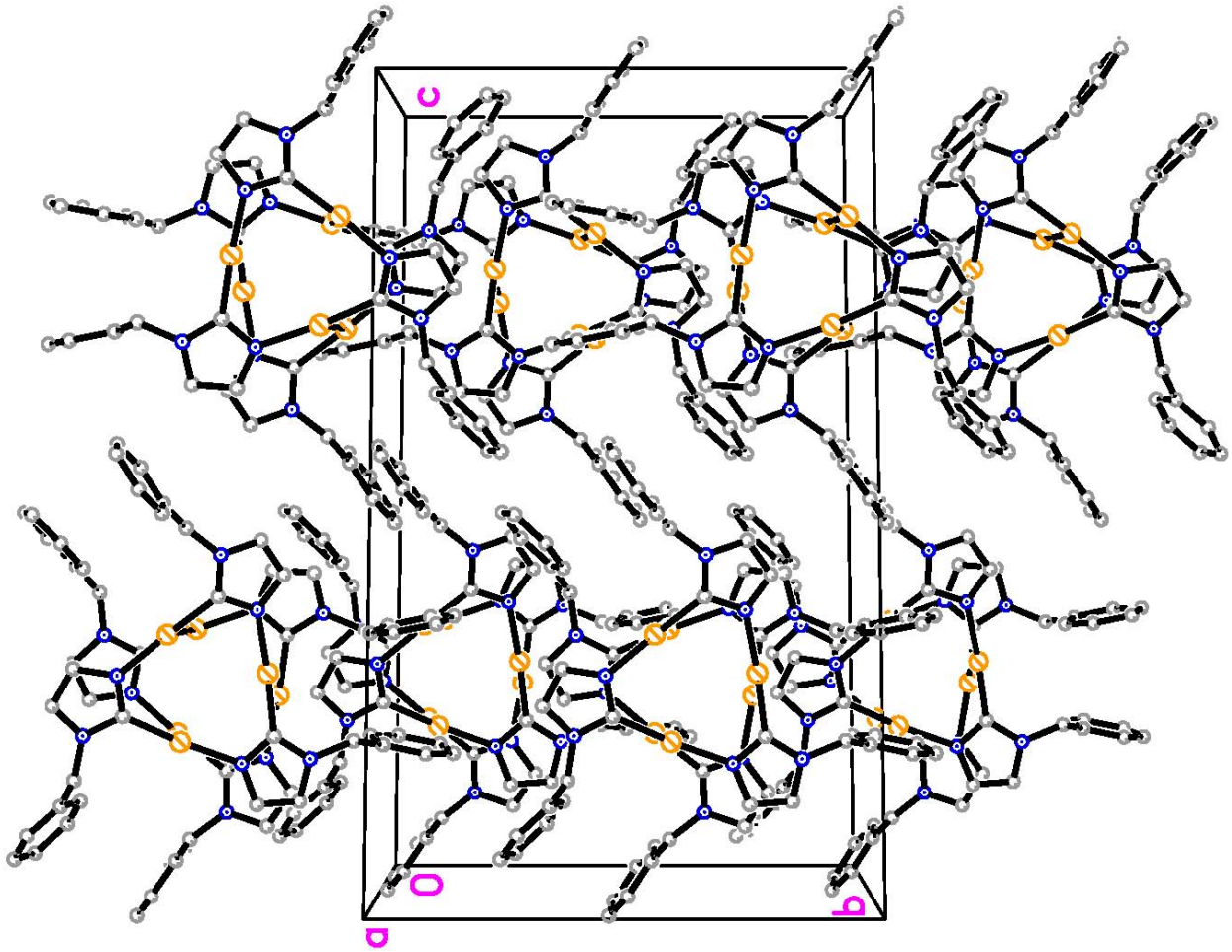

Fig. S2 ORTEP view of the extended molecular packing in **1**.

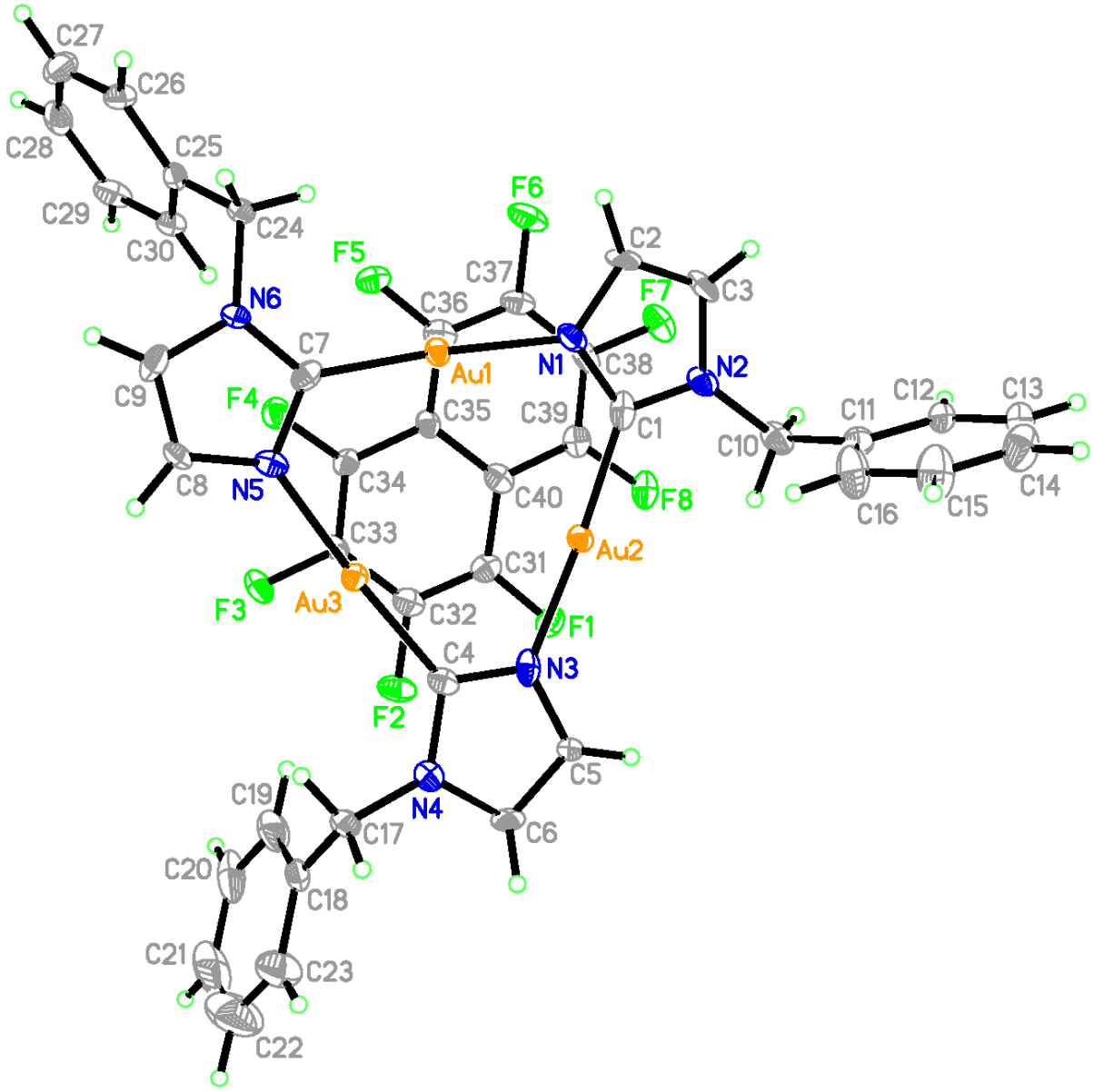

Fig. S3 ORTEP view of the molecular structure of the **1**•$C_{10}F_8$ binary adduct.

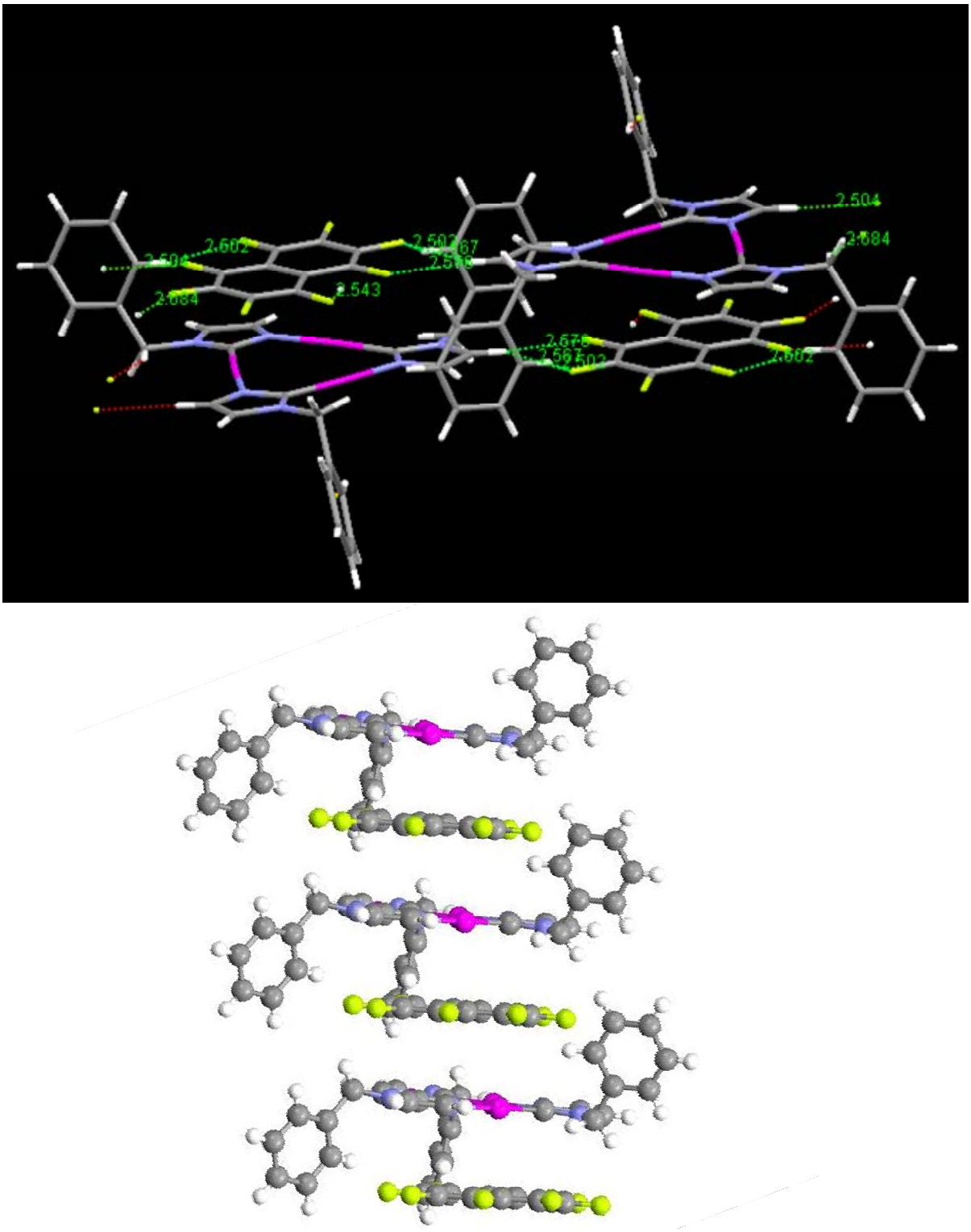

Fig. S4 Additional views of the extended molecular packing in the **1**•$C_{10}F_8$ binary adduct.

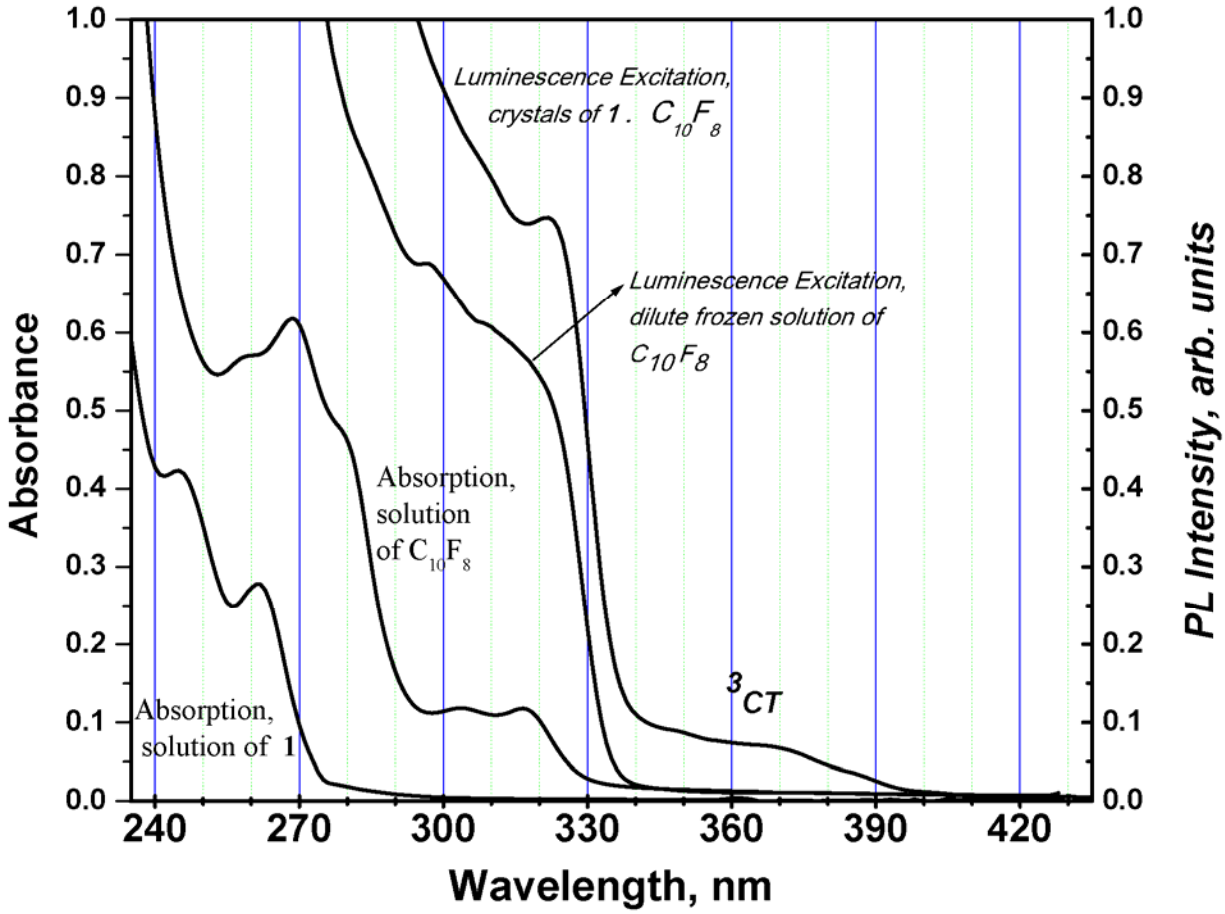

Fig. S5 Overlay of various electronic spectra of **1**, **1**•$C_{10}F_8$ and free $C_{10}F_8$ for purposes of comparison.

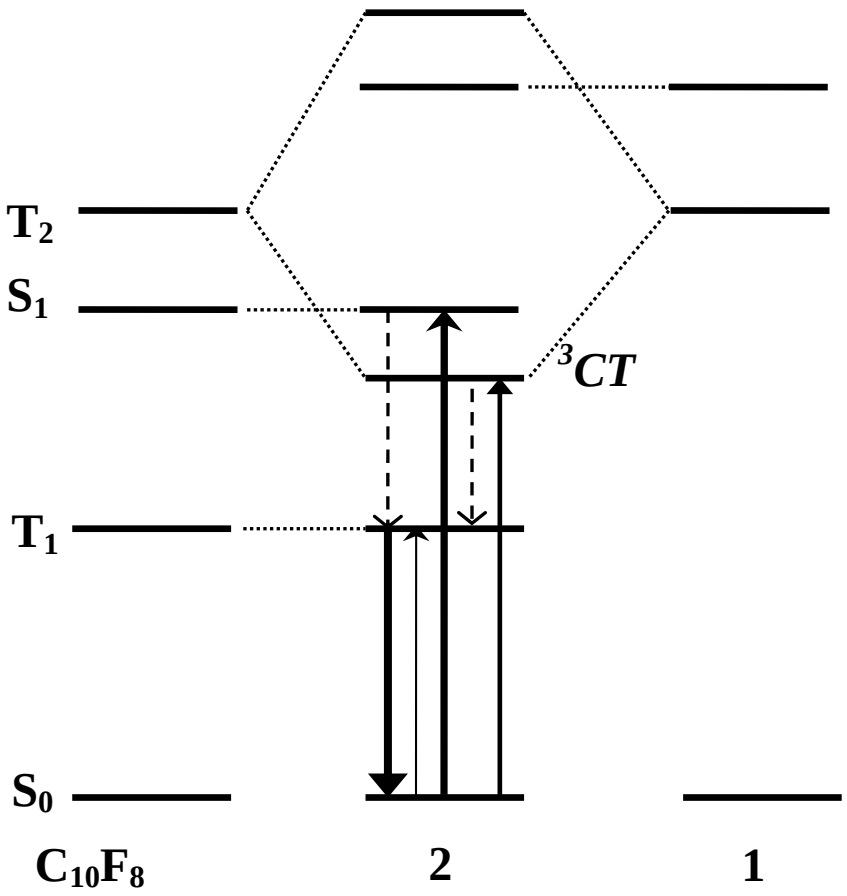

Fig. S6 Energy level diagram showing the interaction between the excited states of **1** and F_8-naphthalene ($C_{10}F_8$) to form a lower-energy charge transfer (CT) state in the **2** adduct. Solid and dashed arrows represent radiative and non-radiative processes, respectively, and the thickness of arrows denoting absorptions represent their relative contribution in the phosphorescence excitation route.

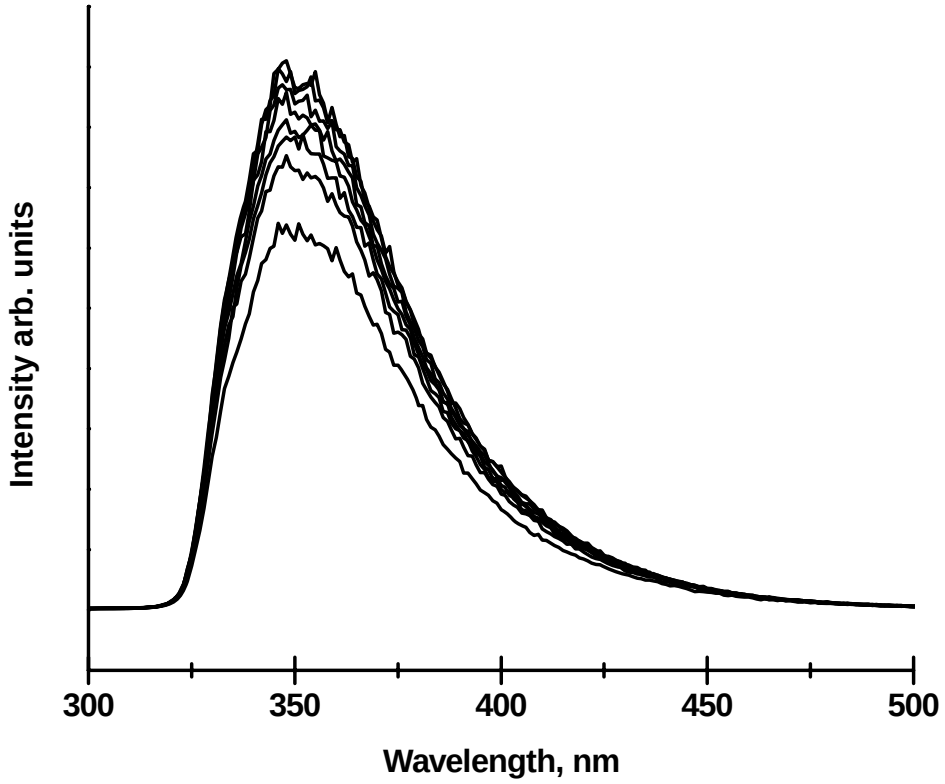

Fig. S7 Fluorescence quenching of F_8-naphthalene as a function of incremental additions of **1** in dichloromethane.

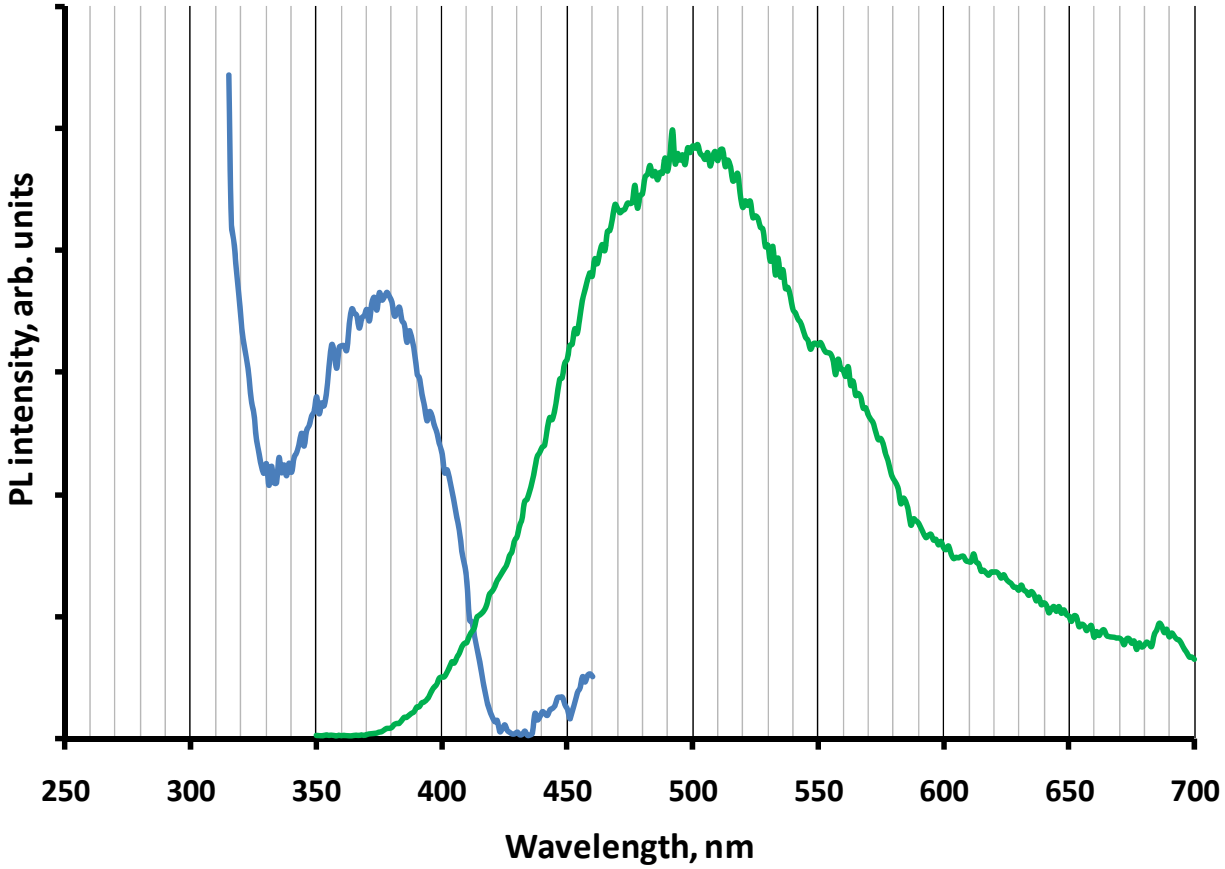

Fig. S8 Photoluminescence spectra (left: excitation; right: emission) of a powder sample of **1** at 77 K. No luminescence was detectable for this powder at ambient temperature and even at 77 K the emission was much weaker than that for the single crystals, albeit the excitation and emission profiles are very similar; compare with Fig. 3 data in the main manuscript.

5. Supplementary Tables

Table S1. Crystal Data and Structure Refinement for **1**.

Empirical formula	$C_{30}H_{27}Au_3N_6$	
Formula weight	1062.48	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 14.3218(11) Å	α= 90°.
	b = 15.3777(12) Å	β= 101.5420(10)°.
	c = 26.223(2) Å	γ = 90°.
Volume	5658.5(8) $Å^3$	
Z	8	
Density (calculated)	2.494 Mg/m^3	
Absorption coefficient	15.549 mm^{-1}	
F(000)	3888	
Crystal size	0.41 x 0.37 x 0.32 mm^3	
Theta range for data collection	2.22 to 27.17°.	
Index ranges	-18<=h<=18, -19<=k<=19, -33<=l<=33	
Reflections collected	34634	
Independent reflections	6282 [R(int) = 0.0442]	
Completeness to theta = 27.17°	99.6 %	
Absorption correction	Multiscan	
Max. and min. transmission	0.0832 and 0.0603	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6282 / 0 / 352	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0259, wR2 = 0.0616	
R indices (all data)	R1 = 0.0351, wR2 = 0.0664	
Largest diff. peak and hole	1.073 and -1.006 $e.Å^{-3}$	

Table S2. Crystal Data and Structure Refinement for **1**•$C_{10}F_8$.

Empirical formula	$C_{40}\ H_{27}\ Au_3\ F_8\ N_6$	
Formula weight	1334.58	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.8775(11) Å	α= 75.829(2)°.
	b = 13.655(2) Å	β= 87.141(2)°.
	c = 20.411(3) Å	γ = 87.703(2)°.
Volume	1855.4(5) $Å^3$	
Z	2	
Density (calculated)	2.389 Mg/m^3	
Absorption coefficient	11.912 mm^{-1}	
F(000)	1236	
Crystal size	0.33 x 0.05 x 0.04 mm^3	
Theta range for data collection	2.05 to 27.13°.	
Index ranges	-8<=h<=8, -17<=k<=17, -26<=l<=26	
Reflections collected	22721	
Independent reflections	8145 [R(int) = 0.0475]	
Completeness to theta = 27.13°	99.2 %	
Absorption correction	Multiscan	
Max. and min. transmission	0.6670 and 0.1107	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8145 / 0 / 514	
Goodness-of-fit on F^2	1.003	
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.1059	
R indices (all data)	R1 = 0.0576, wR2 = 0.1158	
Largest diff. peak and hole	4.148 and -2.609 e.$Å^{-3}$	

6. References

(1) F. Bonati, A. Burini, B. R. Pietroni and B. Bovio, *J. Organomet. Chem.,* 1989, **375**, 147.

(2) Bruker APEX2; Bruker AXS Inc.: Madison, WI, 2007.

(3) Bruker SAINT; Bruker AXS Inc.: Madison, WI, 2007.

(4) Bruker SADABS; Bruker AXS Inc.: Madison, WI, 2007.

(5) Sheldrick, G.M. SHELXTL, v. 2008/3; Bruker Analytical X-ray: Madison, WI, 2008.