Supplementary material.

Materials: adpa was synthesized following a literature method[1]. The metal salts $Cd(NO_3)_2.4H_2O$ (Riedel de Haën) and $CdCl_2.2.5\ H_2O$ (Fisher) were obtained in ≥ 99% purity and used as received. All solutions were made up in deionized water (Milli-Q, Waters Corp.) of > 18 $M\Omega.cm^{-1}$ resistivity, plus HPLC grade methanol from Merck.

Synthesis of Cadmium (II) Complexes of ADPA. The general procedure followed for the synthesis of cadmium(II) complexes with ADPA was as follows: 1 equiv of ADPA (35.0 mg, 0.09 mmol) was dissolved in methanol (3 mL) and added to a solution of 1 equiv of the metal salt ($Cd(NO_3)_2{\bullet}4H_2O$ or $CdCl_2.2.5\ H_2O$) in methanol (3mL and 2mL respectively) in a 20 mL sample vial. The resulting solution was placed standing upright in a jar with a lid, containing diethyl ether to a depth of about 5 mm, and tightly sealed. Diffusion of diethyl ether vapor into the solutions resulted in deposition of pale-yellow crystals over a period of a few hours. The solutions were filtered off under vacuum and the crystals were air-dried. $[Cd(ADPA)(NO_3)_2]$ (**1**): pale-yellow crystals. Elem. anal. calcd. for $C_{27}H_{23}CdN_5O_6$ C, 51.81; N, 11.19. Found C, 51.51; N, 10.94 $[Cd(ADPA)Cl_2]$ (**2**) pale-yellow crystals. Elem. anal. calc. for $C_{27}H_{23}CdCl_2N_3$ C, 56.61; N, 7.34. Found C56.64; N, 7.31.

Fluorescence Measurements: Excitation-emission matrix (EEM) fluorescence properties were determined on a Jobin Yvon SPEX Fluoromax-3 scanning fluorometer equipped with a 150 W Xe arc lamp and a R928P detector. The instrument was configured to collect the signal in ratio mode with dark offset using 5 nm bandpasses on both the excitation and emission monochromators. The EEMs were created by concatenating emission spectra measured every 5 nm from 250 to 500 nm at 51 separate excitation wavelengths. Scans were corrected for instrument configuration using factory supplied correction factors. Post processing of scans was performed using the FluorEssence program.[2] The software eliminates Rayleigh and Raman scattering peaks by excising portions (± 10-15 nm FW) of each scan centered on the respective scatter peak. The excised data is replaced using three-dimensional interpolation of the remaining data according to the Delaunay triangulation method and constraining the interpolation such that all non-excised data is retained. Following removal of scatter peaks, data were normalized to a daily-determined water Raman intensity (275ex / 303em, 5 nm bandpasses). Replicate scans were generally within 5% agreement in terms of intensity and within bandpass resolution in terms of peak location. The fluorescence of the adpa solutions was recorded in 50% MeOH/water, with an excitation wavelength of 350 nm. The titration procedure involved a jacketed external titration cell thermostatted to 25.0 C, with N_2 bubbled through to exclude O_2 and CO_2. 50 mL of the $Cd(ClO_4)_2$/adpa solution (5×10^{-6} M in 50% $MeOH/H_2O$) at pH 6.55 was placed in the cell. A micro-pipette was used to add quantities of 0.5 M NaCl at pH 6.55. pH in the titration cell mas monitored using a VWR symphony SR601C pH meter with a VWR synpHony gel epoxy semimicro combination pH electrode. pH was kept constant at 6.55 by additions of tiny quantities of acid or base whenever very small changes from pH 6.55 were observed. The same procedure was used with NaBr, NaI, $Na_2S_2O_3$, and Na_2SO_4 in studying the binding of these ions to the Cd(II)/adpa complex.

Molecular structure determination:

[Cd(adpa)(NO_3)$_2$] (1): A Leica MZ 7$_5$ microscope was used to identify a suitable colorless multi-faceted crystal with very well defined faces with dimensions (max, intermediate, and min) 0.2mm x 0.2 mm x 0.2 mm from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream maintained at 150K.

An APEXII BRUKER X-ray (three-circle) diffractometer was employed for crystal screening, unit cell determination, and data collection.The goniometer was controlled using the APEX2 software suite[3]. The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The detector was set at 6.0 cm from the crystal sample. The X-ray radiation employed was generated from a Mo sealed X-ray tube (K_α= 0.70173Å with a potential of 40 kV and a current of 40 mA) fitted with a graphite monochromator in the parallel mode (175 mm collimator with 0.5 mm pinholes).

Sixty data frames were taken at widths of 0.5° with an exposure time of 10 seconds. These reflections were used in the auto-indexing procedure to determine the unit cell. A suitable cell was found and refined by nonlinear least squares and Bravais lattice procedures. The unit cell was verified by examination of the *h k l* overlays on several frames of data. No super-cell or erroneous reflections were observed.

After careful examination of the unit cell, a standard data collection procedure was initiated using omega scans. Each frame was exposed for 10 sec and contrasted against a 10 sec. dark current exposure.

Data Reduction, Structure Solution, and Refinement

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2.[3] The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects.[1] Finally the data was merged and scaled to produce a suitable data set. The absorption correction program SADABS[4] was employed to correct the data for absorption effects.

Systematic reflection conditions and statistical tests for the data suggested the space group$P2_1/n$. A solution was obtained readily using SHELXL 2012 (SHELXS).[3] All non-hydrogen atoms were refined with anisotropic thermal parameters. The Hydrogen atoms bound to carbon were placed in idealized positions [C–H = 0.96 Å, U_{iso}(H) = 1.2 x U_{iso}(C)]. The structure was refined (weighted least squares refinement on F^2) to convergence.[5]

[Cd(adpa)Cl_2] (1): A BRUKER D8 GADDS X-ray (three circle) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the FRAMBO software suite[6]. The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The detector was set at 6.0 cm from the crystal sample (MWPC Hi-Star Detector, 512x512 pixel). The X-ray radiation employed was generated from a Cu sealed X-ray tube (K_α= 1.54184Å with a potential of 40 kV and a current of 40 mA) fitted with a graphite monochromator in the parallel mode (175 mm collimator with 0.5 mm mono-capillary optics).

The rotation exposure indicated acceptable crystal quality and the unit cell determination was undertaken. 2100 data frames were taken at widths of 0.5° with an exposure time of 10 seconds. Over 6000 reflections were centered and their positions were determined. These reflections were used in the auto-indexing procedure to determine the unit cell. A suitable cell was found and refined by nonlinear least squares and Bravais lattice procedures and reported here in Table 1. No super-cell or erroneous reflections were observed.

After careful examination of the unit cell, a standard data collection procedure was initiated. This procedure consists of collection of one hemisphere of data collected using omega scans, involving the collection 0.5° frames at fixed angles for ϕ, 2θ, and χ (2θ = -28°, χ= 54.73°, 2θ = -90°, χ= 54.73°), while varying omega. Addition data frames were collected to complete the data set. Each frame was exposed for 5 sec. The total data collection was performed for duration of approximately 24 hours at 110K. No significant intensity fluctuations of equivalent reflections were observed.

Data Reduction, Structure Solution, and Refinement

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program SAINT.[7] The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally the data was merged and scaled to produce a suitable data set. The absorption correction program SADABS[4] was employed to correct the data for absorption effects.

Systematic reflection conditions and statistical tests for the data suggested the space group *P-1*. A solution was obtained readily using SHELXTL (SHELXS).[5] All non-hydrogen atoms were refined with anisotropic thermal parameters. The Hydrogen atoms bound to carbon were placed in idealized positions [C–H = 0.96 Å, $U_{iso}(H) = 1.2 \times U_{iso}(C)$]. The structure was refined (weighted least squares refinement on F^2) to convergence.[5]

Density Functional Theory (DFT) Calculations:

All DFT and time-dependent DFT (TDDFT) calculations were carried out with the *ab initio* quantum chemistry package GAMESS[8] using the B3LYP exchange-correlation functional.[9,10] The SV(P) basis set[11] was used for the main group elements, whereas the Lanl2DZ[12-14] effective core potential was employed for cadmium. All DFT/TDDFT calculations were performed in an aqueous solution environment using a polarizable continuum model (PCM) as implemented in GAMESS.

The geometry optimizations for the ground states of Cd(adpa) complexes were performed with three different initial configurations: (a) X-ray structure in Fig. 3a with two chlorine atoms replaced by two water molecules, (b) X-ray structure in Fig. 3a, and (c) X-ray structure in Fig. 3b with two chlorine atoms (1B and 2B). The importance of Cd-fluorophore interaction can be seen qualitatively in the plots of molecular orbitals (MO) involving Cd. Figure S1 shows the plots of highest occupied MOs containing significant contribution from Cd for the three optimized structures mentioned above. It is evident from the figure that when the chlorine atoms are not bound to Cd, there exists extensive interaction between Cd and fluorophore (Fig. 1S(a)), but, with chlorine bound to Cd, the interaction is negligible (Fig. 1S(b) and (c)).

With the optimized ground state geometries, we investigated the absorptions to the singlet excited states via TDDFT calculations. The excitation energies and oscillator strengths for three Cd(adpa) systems are reported in Table III. For all three systems, the HOMO-LUMO transition is allowed, which is contained mostly within the anthracenyl fluorophore. To investigate the emission process, we optimized the geometries of Cd(adpa) complexes on the excited electronic state (S_1) using the TDDFT method with the same functional and basis set as the ground state calculations. The excited state geometry optimization started from the optimized ground state structures. The intensities of $S_0 \leftarrow S_1$ transition were estimated through TDDFT calculations using the optimized excited state geometries and the results are reported in Table III.

Table 1. Crystal data and structure refinement for [Cd(adpa)(NO_3)$_2$] (**1**).

Empirical formula	C27 H23 Cd N5 O6	
Formula weight	625.90	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 13.613(5) Å	α= 90°.
	b = 11.143(4) Å	β= 94.867(9)°.
	c = 16.466(6) Å	γ = 90°.
Volume	2488.7(15) Å^3	
Z	4	
Density (calculated)	1.670 Mg/m^3	
Absorption coefficient	0.932 mm^{-1}	
F(000)	1264	
Crystal size	0.169 x 0.167 x 0.159 mm^3	
Theta range for data collection	2.028 to 31.977°.	
Index ranges	-20<=h<=20, -16<=k<=16, -24<=l<=24	
Reflections collected	138625	
Independent reflections	8347 [R(int) = 0.0383]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9368 and 0.8340	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8347 / 0 / 352	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0226, wR2 = 0.0558	
R indices (all data)	R1 = 0.0274, wR2 = 0.0582	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.528 and -0.461 e.Å^{-3}	

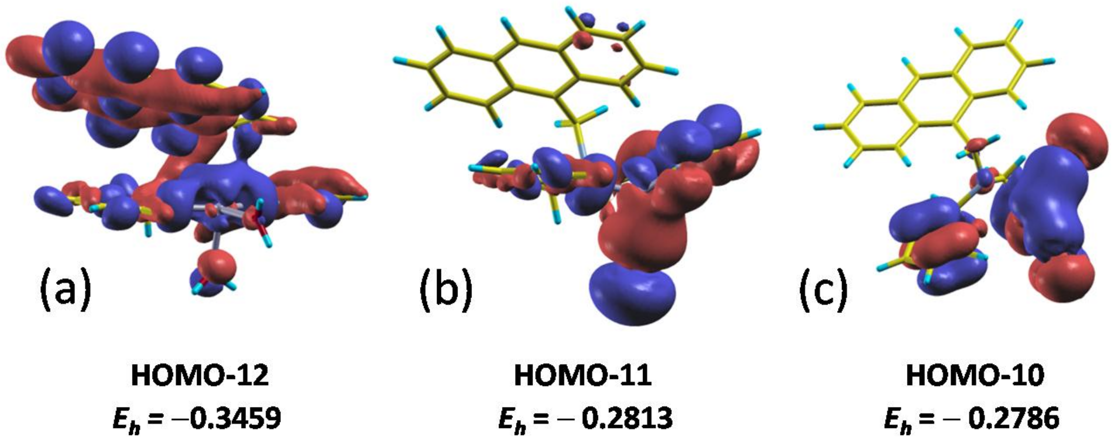
Table 2. Crystal data and structure refinement for [Cd(adpa)Cl_2] (**2**).

Identification code	rh96	
Empirical formula	C27 H23 Cd Cl2 N3	
Formula weight	572.78	
Temperature	110(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.6116(4) Å	α= 102.944(2)°.
	b = 14.3392(5) Å	β= 106.317(3)°.
	c = 16.9902(6) Å	γ = 91.605(3)°.
Volume	2406.63(16) Å^3	
Z	4	
Density (calculated)	1.581 Mg/m^3	
Absorption coefficient	9.464 mm^{-1}	
F(000)	1152	
Crystal size	0.300 x 0.200 x 0.050 mm^3	
Theta range for data collection	2.793 to 64.133°.	
Index ranges	-12<=h<=12, -16<=k<=16, -19<=l<=19	
Reflections collected	46477	
Independent reflections	7718 [R(int) = 0.0651]	
Completeness to theta = 67.679°	88.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7524 and 0.4422	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7718 / 0 / 595	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0444, wR2 = 0.1328	
R indices (all data)	R1 = 0.0517, wR2 = 0.1397	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.710 and -1.281 e.Å^{-3}	

Table III. The electronic excitation energies (eV) and oscillator strengths (*f*) obtained from the TDDFT/B3LYP/SV(P) calculations with the PCM solvation. The TDDFT calculations were performed with the optimized ground state geometries for the absorption and with the optimized singlet excited state geometries for the emission. The ground state structure **a**, **b** and **c** were obtained, respectively, by initiating the geometry optimization with (a) X-ray structure in Fig. 3a with two chlorine atoms replaced by two water molecules, (b) X-ray structure in Fig. 3a, and (c) X-ray structure in Fig. 3b with two chlorine atoms (1B and 2B).

Structure	*Absorption*		*Emission*	
	Energy (eV)	*f*	Energy(eV)	*f*
a	2.97	0.1072	2.51	0.0926
b	3.04	0.1116	2.64	0.1122
c	3.11	0.1382	2.68	0.1342

Figure S1. The highest occupied molecular orbitals (MO) containing significant contribution from Cd for the three structures (structure **a**, **b** and **c**) described in Table III.



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