Supporting Information

Two Selective Fluorescent Chemosensors for Cadmium Ion in 99% Aqueous solution: the End Group Effect on the Selectivity, DFT calculations and Biological Applications

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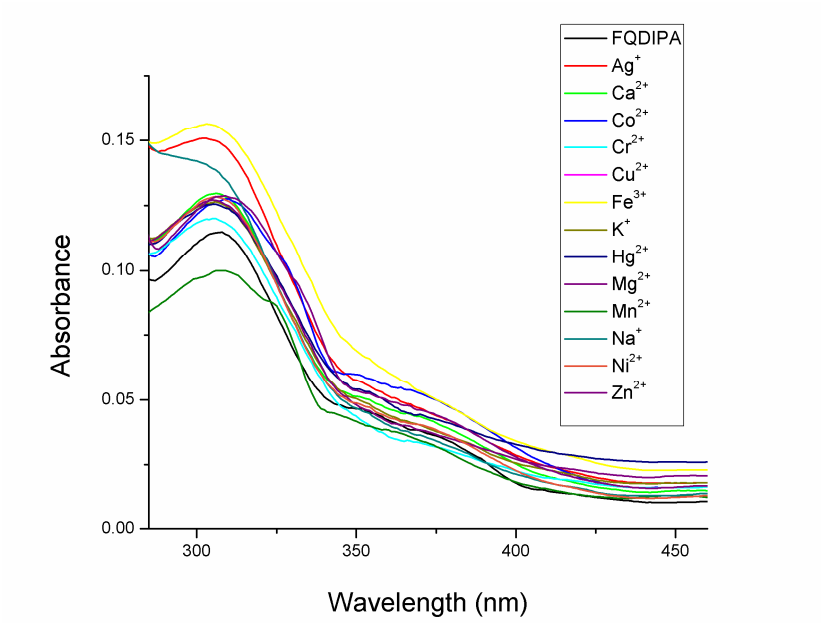


Fig. S1 UV-vis spectral changes of FQDIPA (black lines) upon addition of other cations (coloured lines) in Tris–HCl (50 mM, pH = 7.42) ethanol–H_2O (v/v = 1:99) at room temperature ([FQDIPA] = 0.025 mM, [M^{n+}] = 0.025 mM).

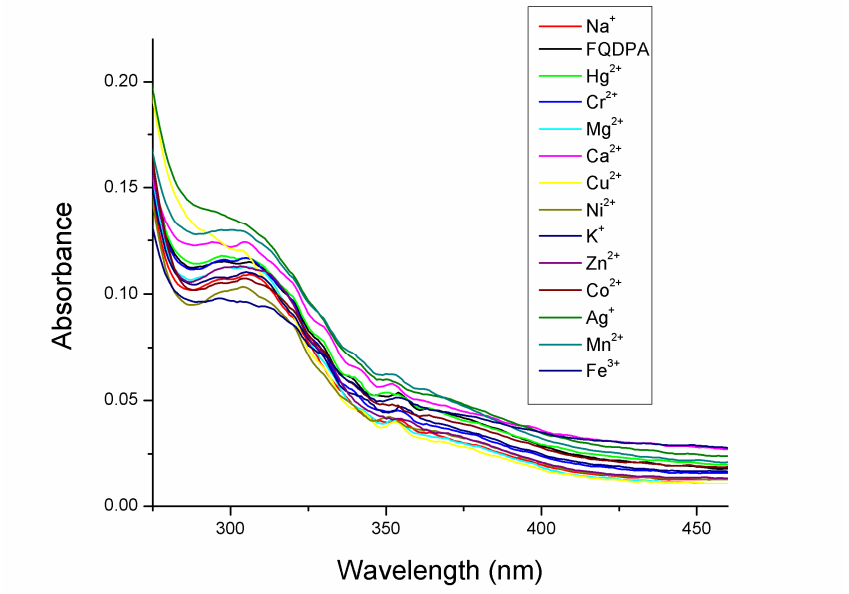


Fig. S2 UV-vis spectral changes of FQDPA (black lines) upon addition of other cations (coloured lines) in Tris–HCl (50 mM, pH = 7.42) ethanol–H_2O (v/v = 1:99) at room temperature ([FQDPA] = 0.025 mM, [M^{n+}] = 0.025 mM).

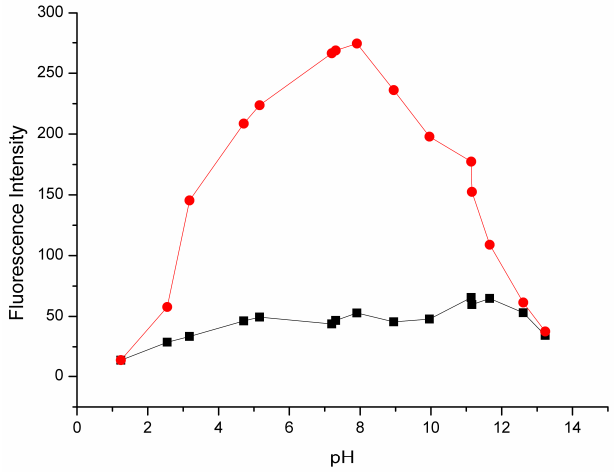


Fig. ~~S1~~ S3 Fluorescence intensities of FQDIPA and Cd-FQDIPA at various pH values at room temperature (λ_{ex} = 305 nm). Red line, the fluorescence intensities at 418 nm of Cd-FQDIPA at various pH ([FQDIPA] = 0.01 mM, [Cd-FQDIPA] = 0.01 mM); black line, the fluorescence intensities at 418 nm of FQDIPA at various pH ([FQDIPA] = 0.01 mM).

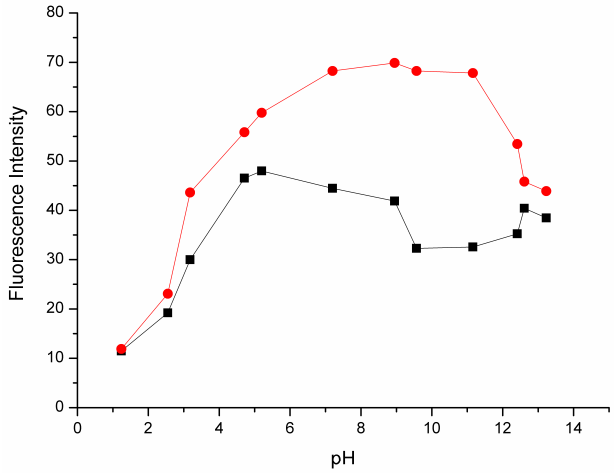


Fig. ~~S2~~ S4 Fluorescence intensities of FQDPA and Cd-FQDPA at various pH values at room temperature (λ_{ex} = 305 nm). Red line, the fluorescence intensities at 418 nm of Cd-FQDPA at various pH ([FQDPA] = 0.01 mM, [Cd-FQDPA] = 0.01 mM); black line, the fluorescence intensities at 418 nm of FQDPA at various pH ([FQDPA] = 0.01 mM).

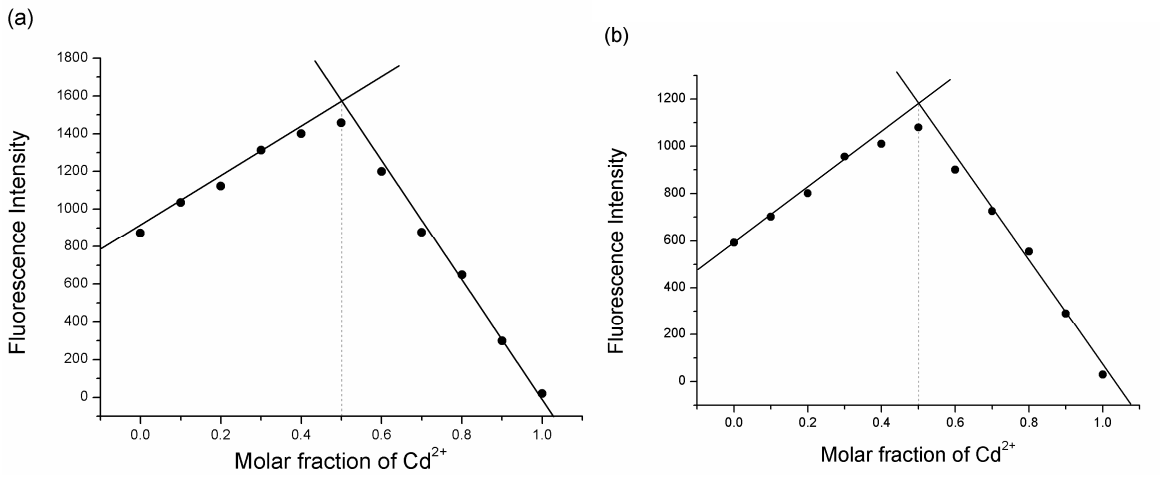


Fig. ~~S3~~ S5 ***Job's*** plots show the 1:1 binding of FQDIPA (a) and FQDPA (b) to Cd^{2+}.

Table S1 The details of the contributions of orbital transitions for some electronic transitions with large oscillator strengths for FQDIPA from the TD-DFT calculation.

Excited State 1:	Percentage(%)	Excitation energy(nm)	Oscillator strength
78 -> 86	27.05	249.04 nm	f=0.3776
80 -> 85	39.77		
83 -> 86	26.13		
84 -> 86	31.40		

Excited State 2:	Percentage(%)	Excitation energy(nm)	Oscillator strength
80 -> 85	16.00	243.66 nm	f=0.2031
83 -> 86	76.76		
84 -> 86	7.237		

Excited State 3:	Percentage(%)	Excitation energy(nm)	Oscillator strength
78 -> 85	3.401	207.43 nm	f=0.2495
80 -> 86	33.88		
84 -> 87	19.97		
84 -> 88	42.74		

Table S2 The details of the contributions of orbital transitions for some electronic transitions with large oscillator strengths for FQDIPA·Cd^{2+} from the TD-DFT calculation.

Excited State 1:	Percentage(%)	Excitation energy(nm)	Oscillator strength
83 -> 90	16.28	276.74 nm	f=0.2385
87 -> 90	16.02		
87 -> 92	2.723		
89 -> 92	64.97		

Excited State 2:	Percentage(%)	Excitation energy(nm)	Oscillator strength
83 -> 90	74.75	266.52 nm	f=0.1197
85 -> 90	4.858		
86 -> 91	2.945		
87 -> 90	2.341		
87 -> 92	2.825		
89 -> 92	12.28		

Excited State 3:	Percentage(%)	Excitation energy(nm)	Oscillator strength
77 -> 91	17.56	206.48 nm	f=0.3276
79 -> 91	5.427		
83 -> 90	2.7121		
87 -> 92	30.69		
88 -> 93	14.25		
89 -> 93	2.281		
89 -> 94	24.17		
89 -> 95	2.903		

Table S3 The details of the contributions of orbital transitions for some electronic transitions with large oscillator strengths for FQDPA from the TD-DFT calculation.

Excited State 1:	Percentage(%)	Excitation energy(nm)	Oscillator strength
93 ->101	39.91	253.96 nm	f=0.3244
95 ->102	6.765		
97 ->103	2.872		
98 ->102	14.98		
98 ->103	3.480		
99 ->102	29.21		
99 ->103	2.777		

Excited State 2:	Percentage(%)	Excitation energy(nm)	Oscillator strength
93 ->101	9.601	250.68 nm	f=0.1227
94 ->103	2.803		
97 ->102	3.331		
97 ->103	8.3		
98 ->102	19.19		
98 ->103	13.42		
99 ->102	5.219		
100 ->103	9.626		
100 ->105	24.94		
100 ->107	3.572		

Excited State 3:	Percentage(%)	Excitation energy(nm)	Oscillator strength
94 ->103	3.526	243.54 nm	f=0.1976
96 ->103	2.905		
97 ->102	3.775		
97 ->103	3.258		
99 ->103	24.02		
99 ->104	3.124		
100 ->103	15.36		
100 ->105	44.03		

Table S4 The details of the contributions of orbital transitions for some electronic transitions with large oscillator strengths for FQDPA·Cd^{2+} from the TD-DFT calculation.

Excited State 1:	Percentage(%)	Excitation energy(nm)	Oscillator strength
94 ->106	17.21	277.16 nm	f=0.2128
99 ->106	15.92		
99 ->108	2.787		

101 ->108	64.09		

Excited State 2:	Percentage(%)	Excitation energy(nm)	Oscillator strength
93 ->106	3.114	266.88 nm	f=0.1294
94 ->106	74.14		
96 ->106	2.154		
99 ->106	3.004		
99 ->108	2.772		
101 ->108	14.81		

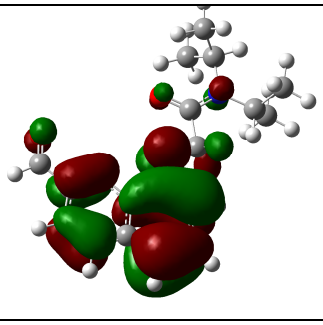
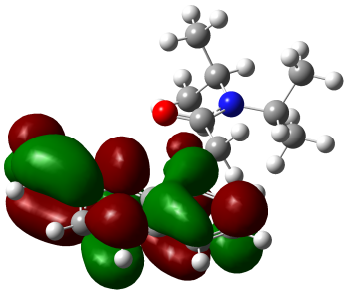
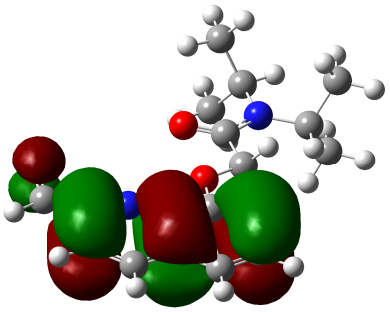
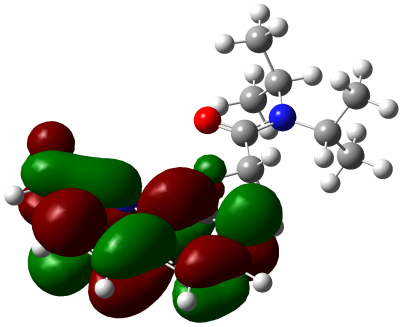
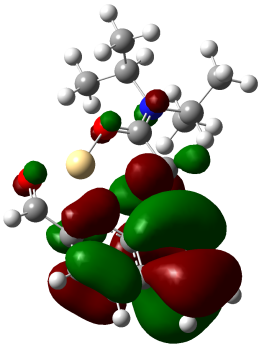
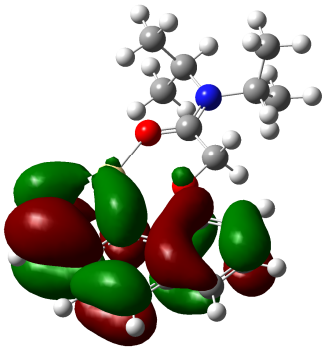
Excited State 3:	Percentage(%)	Excitation energy(nm)	Oscillator strength
105 ->109	96.8645	316.40 nm	f=0.1059
105 ->110	3.1354		

Table S5 Atomic orbital contribution to some frontier molecular orbitals of FQDIPA·Cd^{2+}

Molecular orbital	Cd(46)	N(1)	O(43)	O(44)	O(45)
H-4	0.0256	0.000209	0.9708	0.000600	0.000296
H-3	1.547	1.061	22.87	0.1153	0.00658
H-2	0.1125	0.4696	0.00126	1.007	6.232
H-1	0.5979	0.1434	21.53	0.0464	0.034
HOMO	0.2726	5.327	0.5983	15.05	0.8284
LUMO	2.383	16.55	0.1063	0.5112	17.89
L+1	64.31	6.816	9.443	2.194	8.678
L+2	0.3337	5.821	0.00159	0.4617	4.856
L+3	21.26	0.4185	2.644	1.249	0.0225
L+4	3.496	0.7893	1.53	0.227	6.368

Table S6 Atomic orbital contribution to some frontier molecular orbitals of FQDPA·Cd^{2+}

Molecular orbital	Cd(2)	N(1)	O(23)	O(24)	O(25)
H-4	0.3048	5.362	0.1754	15.17	0.8346
H-3	0.1073	0.04484	0.2635	0.4551	0.00718
H-2	0.01079	0.01884	0.09894	0.5427	0.00724
H-1	0.1379	0.01313	0.6085	0.022	0.00593
HOMO	0.2109	0.02916	3.316	0.5064	0.01086
LUMO	2.358	16.6	0.1028	0.5292	17.93
L+1	64.46	6.883	9.394	2.158	8.686
L+2	0.3368	5.823	0.00608	0.4533	4.848
L+3	16.48	0.436	5.2012	1.485	0.02352
L+4	0.2035	0.3439	2.784	0.9895	4.563

FQDIPA		
	HOMO	LUMO
		
	HOMO-4	LUMO+1
$FQDIPA \cdot Cd^{2+}$		
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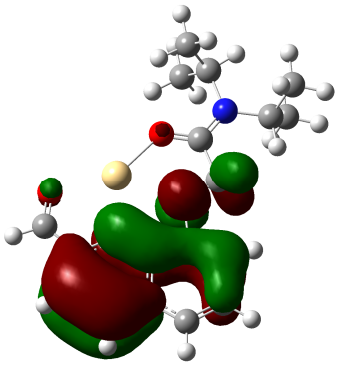
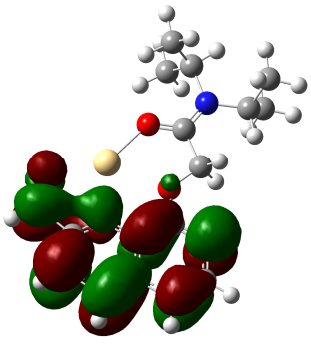
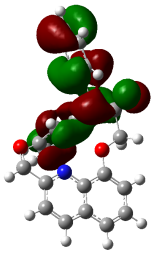
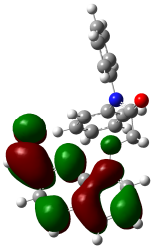
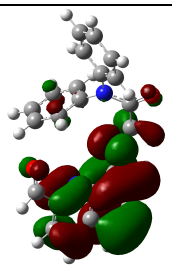
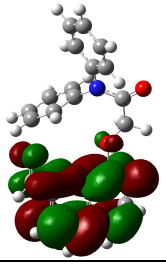
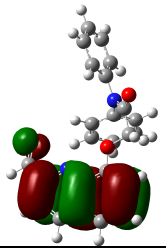
		
	HOMO-6	LUMO+2

Fig. S64 Frontier molecular orbitals including HOMO and LUMO of FQDIPA and $FQDIPA \cdot Cd^{2+}$

FQDPA		
	HOMO	LUMO
		
	HOMO-1	LUMO+1
		
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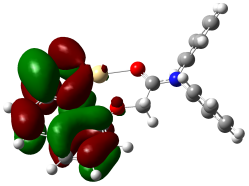
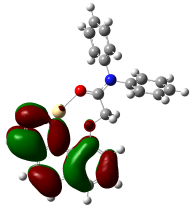
$FQDPA{\cdot}Cd^{2+}$		
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	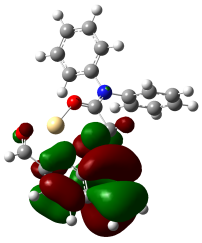	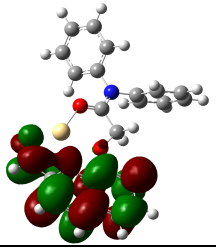
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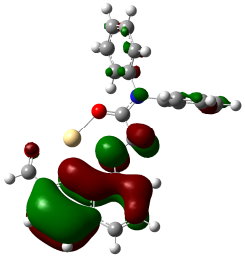
		
	HOMO-11	

Fig. S75 Frontier molecular orbitals including HOMO and LUMO of FQDPA and $FQDPA{\cdot}Cd^{2+}$

Table S7 Electronic energies and Cartesian coordinates of FQDIPA

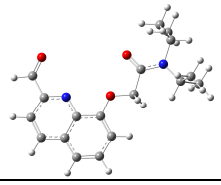
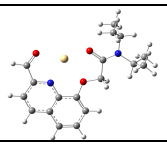
Energy = -1034.32895041 a.u = -28145.7457 eV = -649051.2425 kcal/mol			
N	-2.75511000	0.89960200	0.00017100
C	1.97208800	0.39691000	-0.00062700
C	0.96564500	-0.77678400	-0.00012900
H	1.10889300	-1.40789400	0.88898600
H	1.10882700	-1.40841200	-0.88889500
C	-1.38270600	-1.07385800	-0.00020900
C	-1.29013300	-2.45519400	-0.00032200
H	-0.32397300	-2.94491800	-0.00033300
C	-2.45664500	-3.25891400	-0.00043300
H	-2.34122700	-4.33948600	-0.00054500
C	-3.71198600	-2.70173700	-0.00040700
H	-4.60261800	-3.32411500	-0.00050600
C	-3.84981500	-1.28955000	-0.00022300
C	-2.68569900	-0.44856700	-0.00009200
C	-3.95288500	1.46601700	0.00027500
C	-5.16618900	0.73107600	0.00010000
H	-6.11782900	1.25613900	0.00017400
C	-5.10952700	-0.64179300	-0.00013700
H	-6.01587100	-1.24260900	-0.00025100
C	-4.03069100	2.96152300	0.00062900
H	-5.07599000	3.35049300	0.00056800
C	4.30864500	1.17357100	-0.00040500
H	5.27827600	0.66686800	0.00017900
C	4.24088000	2.02515600	-1.27709800
H	3.29843800	2.57261800	-1.32844300
H	5.06728800	2.74552900	-1.28210800
H	4.33231500	1.39843000	-2.17107600
C	4.24009300	2.02654300	1.27532300
H	4.33106000	1.40079700	2.17003600
H	5.06645600	2.74697000	1.28002100
H	3.29759300	2.57400900	1.32553900
C	3.81415900	-1.31719400	0.00093300
H	2.94307200	-1.97415900	0.00086700
C	4.60905900	-1.64125500	1.27736100
H	4.00623300	-1.44798000	2.17077100
H	4.90034200	-2.69776800	1.28015300
H	5.52564600	-1.04647300	1.35056400
C	4.61029800	-1.64276000	-1.27434400
H	5.52707500	-1.04824300	-1.34727600
H	4.90138300	-2.69933000	-1.27568500
H	4.00840800	-1.45036200	-2.16857300
N	3.30750700	0.07102900	-0.00011000
O	1.56433300	1.54767900	-0.00148200
O	-0.33346900	-0.22331800	-0.00019100
O	-3.08562900	3.71643100	0.00095300

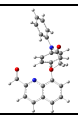
Table S8 Electronic energies and Cartesian coordinates of FQDIPA·Cd^{2+}

Energy = -1081.91859389 a.u = -29440.7360 eV = -678914.1959 kcal/mol			
N	2.49596000	-0.38065900	0.00001300
C	-2.05958100	0.15663900	-0.00005700
C	-1.12262200	1.38941300	-0.00010400
H	-1.28192900	2.00111400	0.89468100
H	-1.28203500	2.00112500	-0.89486300
C	1.32076900	1.69645600	-0.00008400
C	1.34286600	3.06741000	-0.00007800
H	0.42764800	3.64958200	-0.00015100
C	2.59683700	3.74828400	0.00001700
H	2.58869800	4.83347700	0.00002000
C	3.79784100	3.07476400	0.00009800
H	4.73688100	3.61860000	0.00016500
C	3.80823900	1.65490800	0.00009600
C	2.55052300	0.96228500	0.00000800
C	3.60947000	-1.11682800	0.00009200
C	4.88893900	-0.53045600	0.00017400
H	5.78016300	-1.15036500	0.00023600
C	4.97761100	0.85541900	0.00017700
H	5.95120600	1.33717000	0.00024200
C	3.35761800	-2.57646400	0.00008900
H	4.21244800	-3.26461800	0.00014600
C	-4.31126800	-0.85249100	0.00004700
H	-5.29600000	-0.38479100	0.00001300
C	-4.19535000	-1.68078700	-1.28461700
H	-3.25514100	-2.23432000	-1.33378300
H	-5.01388400	-2.40699600	-1.30382400
H	-4.28743800	-1.05342100	-2.17658900
C	-4.19538000	-1.68064700	1.28480500
H	-4.28748100	-1.05318100	2.17670500
H	-5.01391800	-2.40685000	1.30407700
H	-3.25517400	-2.23418000	1.33405000
C	-3.99607800	1.69889000	0.00001600
H	-3.17808800	2.42146100	0.00003600
C	-4.80642900	1.92929600	1.28217700
H	-4.19759800	1.77345300	2.17864600
H	-5.16423300	2.96339100	1.29091200
H	-5.68572600	1.28150200	1.34266700
C	-4.80641900	1.92934500	-1.28214100
H	-5.68571000	1.28154500	-1.34266800
H	-5.16423400	2.96343700	-1.29083600
H	-4.19758000	1.77354600	-2.17861200
N	-3.36488000	0.33123900	-0.00000700
O	-1.54529500	-1.01727100	-0.00004700
O	0.21021900	0.87975400	-0.00019000
O	2.21177000	-3.04717300	0.00002200

Cd	0.52234400	-1.50499700	-0.00008100

Table S9 Electronic energies and Cartesian coordinates of FQDPA

Energy = -1260.55402993 a.u
= -34301.6920 eV
= -791009.6290 kcal/mol



N	2.18230500	0.97308700	-0.63982100
C	-1.59277600	-1.91550200	-0.59558800
C	-0.15978100	-2.33702800	-0.23870700
H	0.07733700	-3.16561400	-0.91268100
H	-0.07611800	-2.68030900	0.80096100
C	2.03828400	-1.40189300	-0.33551200
C	2.66713700	-2.61025300	-0.09929700
H	2.08995300	-3.51967300	0.01918100
C	4.07989200	-2.67966100	-0.02157500
H	4.54104500	-3.64685900	0.15867800
C	4.86683200	-1.56265100	-0.17427900
H	5.94984000	-1.62882000	-0.11951500
C	4.25637700	-0.30212200	-0.39896200
C	2.82590100	-0.20033400	-0.47039300
C	2.90588600	2.07646000	-0.75992500
C	4.32405000	2.08657000	-0.74183700
H	4.86252000	3.02299600	-0.86150200
C	4.99167100	0.89903900	-0.55513200
H	6.07783900	0.86557700	-0.52030900
C	2.17616300	3.37330900	-0.89182300
H	2.83675200	4.24631900	-1.09436800
N	-2.09200000	-0.77622900	0.01038700
O	-2.21731700	-2.58287900	-1.40669900
O	0.70533800	-1.22881800	-0.46256000
O	0.97716000	3.51831200	-0.77819900
C	-3.33628300	-0.20551900	-0.43307300
C	-3.62565900	-0.09279000	-1.79932800
C	-4.25095300	0.27956500	0.50847800
C	-4.82275200	0.49011300	-2.20855900
H	-2.92272600	-0.46732500	-2.53261300
C	-5.44360900	0.86833500	0.08788300
H	-4.02767800	0.20186900	1.56712800
C	-5.73761700	0.97433200	-1.27101300
H	-5.03630600	0.57176400	-3.27096100
H	-6.14361400	1.24176000	0.83058500
H	-6.66754600	1.43144300	-1.59763900
C	-1.45677000	-0.17659900	1.16045100
C	-0.81759200	1.06027500	1.03869300
C	-1.51756600	-0.82046300	2.40075600
C	-0.24205900	1.64843300	2.16350800
H	-0.73584900	1.54209600	0.07124700
C	-0.92961300	-0.22967400	3.52160400
H	-2.03559500	-1.77246400	2.48404600
C	-0.29613000	1.00834600	3.40450700
H	0.26078100	2.60502900	2.05697700
H	-0.97858700	-0.73220400	4.48388500

H	0.15616600	1.47175900	4.27735000

Table S10 Electronic energies and Cartesian coordinates of FQDPA·Cd^{2+}

Energy = -1308.13327397 a.u
= -35596.3994 eV = -820866.0567 kcal/mol

N	-3.23114900	-0.40490900	-0.00067600
C	1.31932000	-0.05027900	-0.06691400
C	0.45099600	1.22045800	-0.00660000
H	0.54841700	1.80861500	-0.92424200
H	0.74805300	1.84047400	0.84555700
C	-1.97625500	1.62153600	0.13293700
C	-1.94572000	2.99164100	0.18694500
H	-1.00783600	3.53505700	0.23130100
C	-3.17192100	3.72046900	0.19423300
H	-3.12211100	4.80362600	0.23937700
C	-4.39825500	3.09506600	0.15271200
H	-5.31562000	3.67457700	0.16525000
C	-4.46342200	1.67833700	0.09087500
C	-3.23327000	0.93728300	0.07504100
C	-4.37255300	-1.09496000	-0.05388200
C	-5.62824600	-0.45955200	-0.03164800
H	-6.54269800	-1.04319400	-0.07242300
C	-5.66294200	0.92670400	0.03866400
H	-6.61685400	1.44613500	0.05241800
C	-4.17925900	-2.56052200	-0.14148900
H	-5.06144100	-3.21206100	-0.18214800
N	2.63536400	0.09731500	-0.02910500
O	0.78095800	-1.20391600	-0.14064400
O	-0.89770300	0.76594700	0.14158500
O	-3.05358800	-3.07648300	-0.17115300
Cd	-1.30315500	-1.60543600	-0.09008800
C	3.52607600	-1.05834600	0.01889600
C	3.46640800	-1.93144300	1.10745000
C	4.46157700	-1.22941600	-1.00229200
C	4.35612500	-3.00435000	1.16290600
H	2.75001200	-1.76816300	1.90699400
C	5.34388900	-2.30812800	-0.93556800
H	4.50629300	-0.53159700	-1.83229500
C	5.29189600	-3.19438400	0.14299800
H	4.32477600	-3.68409300	2.00870500
H	6.07430100	-2.45105100	-1.72556300
H	5.98564200	-4.02771500	0.19316400
C	3.24372200	1.42174800	-0.02967000
C	3.84080600	1.89015500	1.14432600
C	3.27290100	2.17088300	-1.21021400
C	4.45892400	3.14077400	1.13555700
H	3.83621000	1.27838100	2.04137600
C	3.89608700	3.42089100	-1.20535400
H	2.84481200	1.77094300	-2.12589800
C	4.48511400	3.90526700	-0.03502200
H	4.92886800	3.51255000	2.04059900
H	3.93509900	4.00513700	-2.11942800

H	4.97668900	4.87310100	-0.03770400

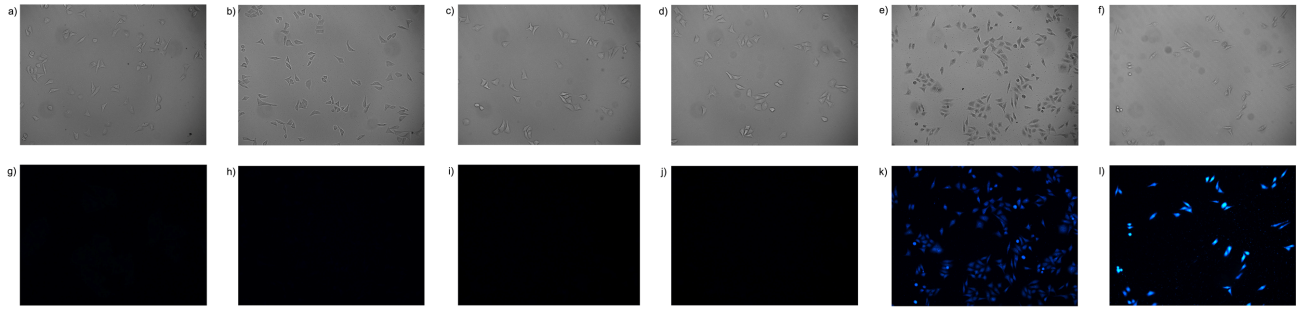


Fig. S~~8~~6 Fluorescence images of Cd^{2+} in HeLa cells incubated with FQDPA and FQDIPA (100 μM). (a), (b), (c), (d), (e), (f) Bright-field transmission image of HeLa cells. (g), (h), (i), (j), (k), (l) Fluorescnece image of HeLa cells. (a)(g) Only HeLa cells. (b)(h) HeLa Cells incubated with 100 μM Cd^{2+} for 20 min. (c)(i) HeLa cells incubated with 100 μM FQDPA for 10min, washed three times with PBS. (d)(j) HeLa cells incubated with 100 μM FQDIPA for 10min, washed three times with PBS. (e)(k) HeLa cells incubated with 100 μM FQDPA for 10min, and then added 100 μM Cd^{2+} for 10 min, washed three times with PBS. (f)(l) HeLa cells incubated with 100 μM FQDIPA for 10min, then added 100 μM Cd^{2+} for 10 min, washed three times with PBS (Zeiss Leica DM 4000B microscope, 10×objective lens).

Cell incubation and imaging

HeLa cells were cultured in DMEM (Hyclone) supplemented with 10% FBS (Gibco). One day before imaging, cells were seeded in 6-well flat-bottomed plates (Costar). The next day, the HeLa cells were incubated with different condition (Fig. 8 and Fig. ~~S6~~S8). All of the cells rinsed with PBS three times, then the fluorescence imaging of cell was observed under 340-380 nm by Zeiss Leica DM 4000B microscope. For all images, the microscope settings, such as brightness, contrast, and exposure time were held constant to compare the relative intensity of Cd^{2+} fluorescence.