Supporting Informations for

Zn^{2+}-Induced Conformational Changes in a Binaphthyl-Pyrene Derivative Monitored by Using Fluorescence and CD Spectroscopy

Fang Wang,[‡,a,d] *Jong Hun Moon,*[‡b] *Raju Nandhakumar,*[‡a,c] *Baotao Kang,*[b]
Dabin Kim,[a] *Kwan Mook Kim*[*a] *Jin Yong Lee*[*c] *and Juyoung Yoon*[*a]

[a]*Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Korea*

[b]*Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea*

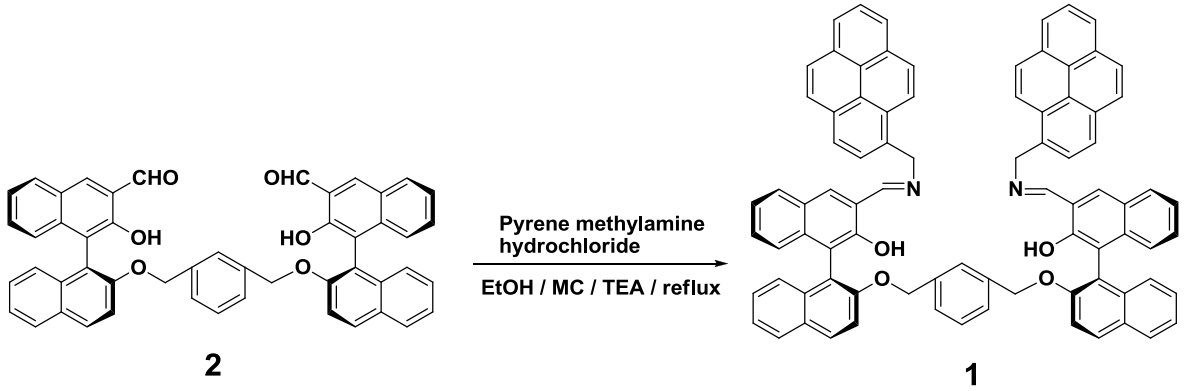
[c]*Department of chemistry, Karunya University, Karunya Nagar, Coimbatore-641 114.TamiNadu, INDIA*

[d]*Department of Chemistry, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing 210009, China*

jyoon@ewha.ac.kr; jinylee@skku.edu; kkmook@ewha.ac.kr

†These authors contributed equally

Synthetic Scheme :



2 1

Synthesis of compound 1 :

Compound **2**[1] (0.300 g, 4.11 mmol), Pyrene methylamine hydrochloride (0.242 g, 0.90 mmol) and triethylamine (0.125 g, 1.23 mmol) were dissolved in a co-solvent of absolute ethanol (25 mL) and methylene chloride (5 mL). The mixture was degassed with nitrogen and then heated under reflux for five hours. After cooled to room temperature, the precipitate was separated and washed with ethanol (ice cold) several times to afford the desired product **1**.

MP : 205 ^{0}C, Yield : 80%

^{1}H NMR ($CDCl_3$, 250 MHz) : δ (ppm): 13.17 (s, 2H), 8.28 (s, 2H), 8.03 (d, 2H, *J*=7.32), 7.97-7.91(m, 4H), 7.87-7.78 (m, 12H), 7.66-7.57 (m, 6H), 7.29-7.13 (m, 14H), 6.56 (s, 3H), 6.36 (s, 1H), 5.17 (q, 4H), 4.70 (s, 4H). ^{13}C NMR ($CDCl_3$, 62.9 MHz) : δ (ppm): 165.67, 154.64, 154.23, 137.22, 135.53, 133.93, 133.36, 131.14, 130.86, 130.78, 130.63, 129.57, 128.81, 128.69, 128.16, 128.00, 127.34, 127.27, 126.83, 126.57, 125.93, 125.60, 125.34, 125.21, 125.06, 124.82, 124.71, 124.57, 123.85, 123.25, 122.79, 120.98, 119.96, 117.43, 115.96, 70.93, 60.64.FAB-MS m/z= 1157.4326 $(M+H)^{+}$, calcd for $C_{84}H_{56}N_2O_4$=1156.4240.

[1]Y.Zhou, J. Kim, R.Nandhakumar, M. Kim, E. Cho, Y. Kim, C. Lee, S. Han, D. Kim, K. Kim, J. Kim,J. Yoon. *Chem. Comm.*,**2010**.46.6512-6514

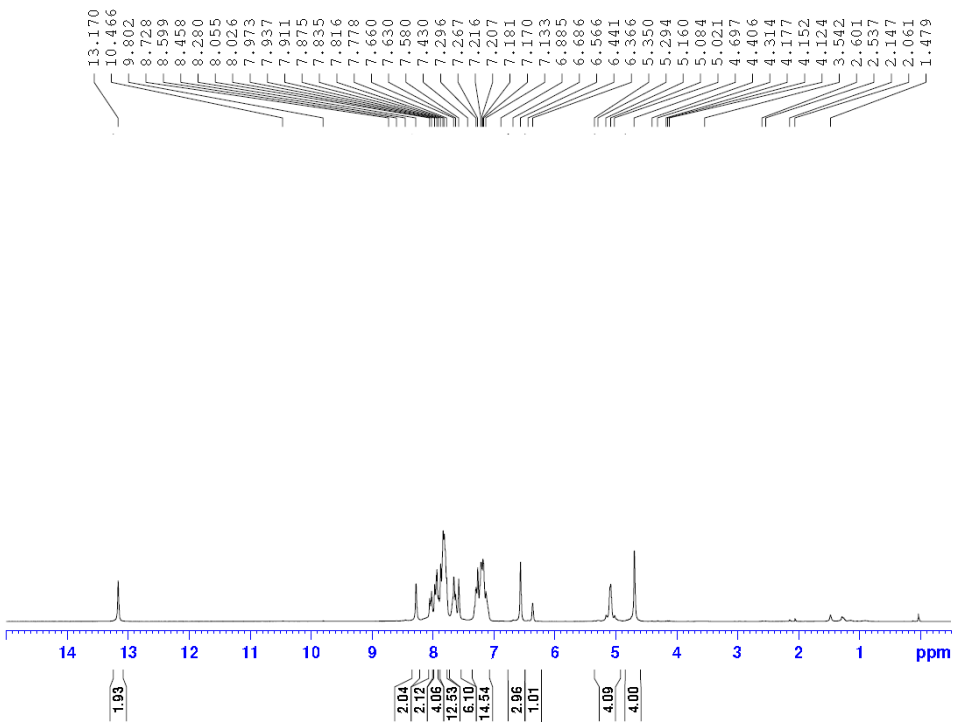


Figure S1. ^{1}H NMR (250 MHz) spectrum of compound **1**.

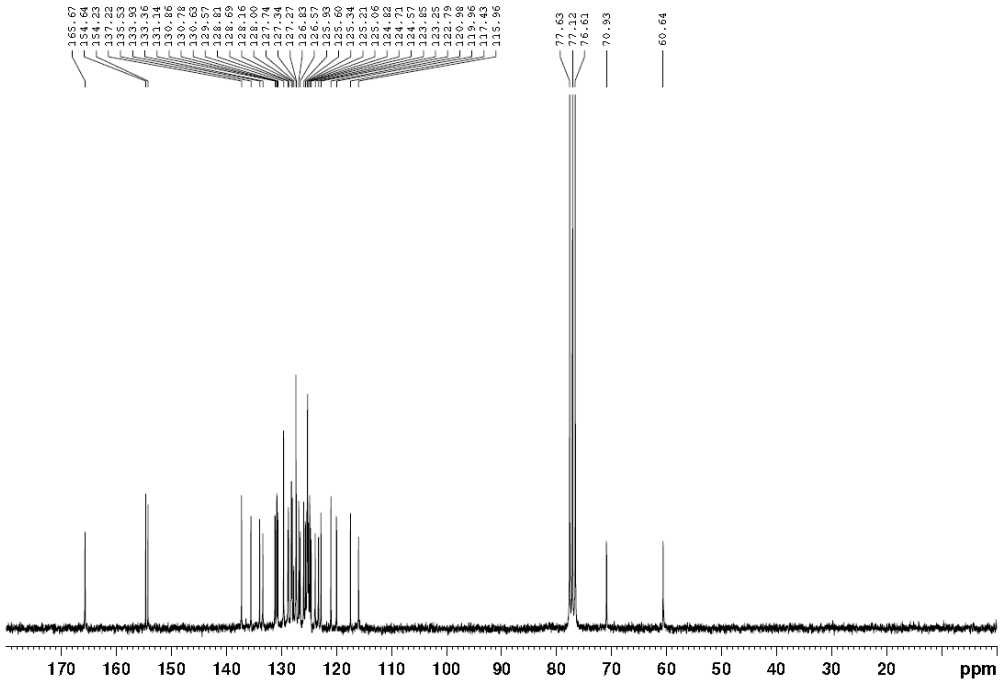


Figure S2. ^{13}C NMR (62.9 MHz) spectrum of compound **1**.

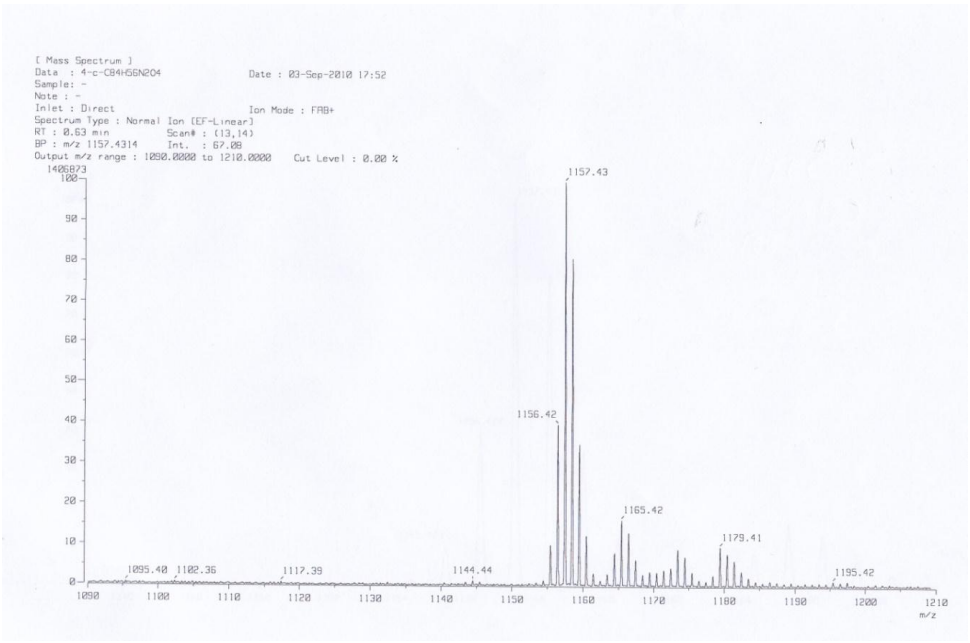


Figure S3. Fab mass of compound **1**.

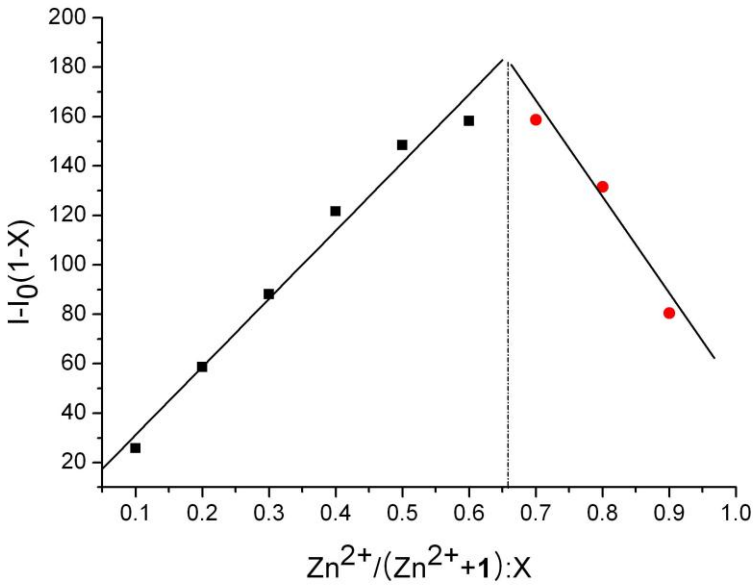


Figure S4: Fluorescence at 559 nm of **1** and Zn^{2+} in DMSO-HEPES buffer (0.02 M, pH = 7.4) (9:1, v/v) with a total concentration of [**1**] + [Zn^{2+}] = 100μM, indicating a 2:1 metal-ligand ratio of thecomplexation between **1** and Zn^{2+}.

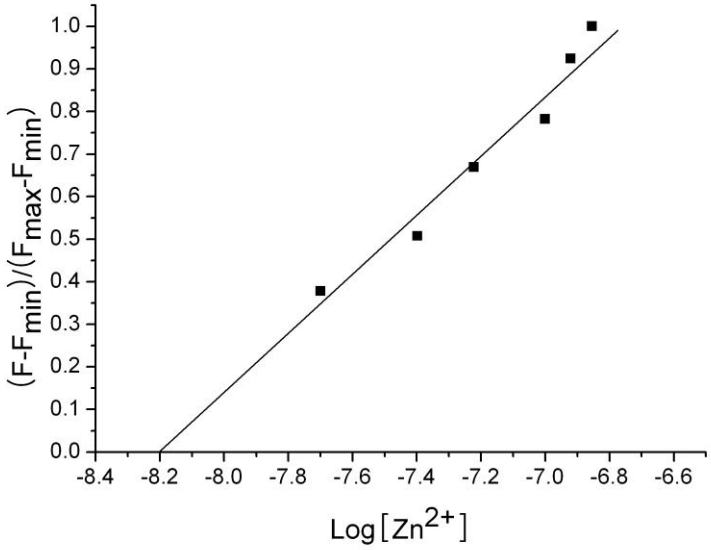


Figure S5: Normalized fluorescene response of **1** (0.1 μM) to changing Zn^{2+} concentrations in DMSO-HEPES buffer (0.02 M, pH = 7.4) (9:1, v/v)

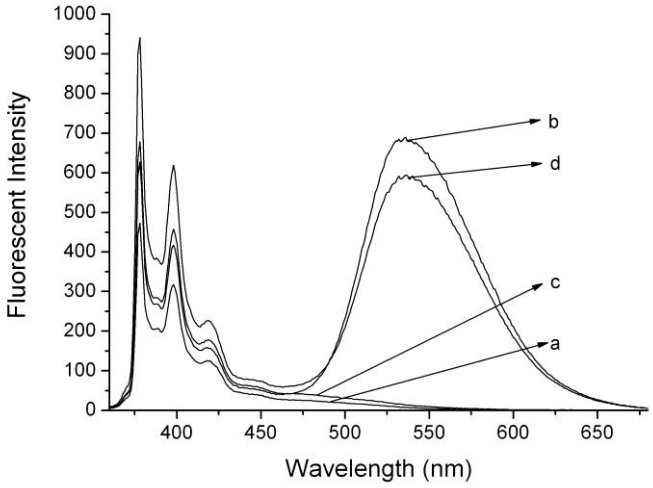


Figure S6. Reversible responses of **1** to Zn^{2+} in DMSO-HEPES buffer (0.02 M, pH = 7.4) (9:1, v/v): (a) 10 μM **1**; (b) 10 μM **1** with 100 μM Zn^{2+}; (c) 10 μM **1** with 100 μM Zn^{2+} and then addition of 20 μM EDTA (sodium salt); (d) 10 μM **1** with 100 μM Zn^{2+}, 20 μM EDTA and then addition of 200 μM Zn^{2+}.

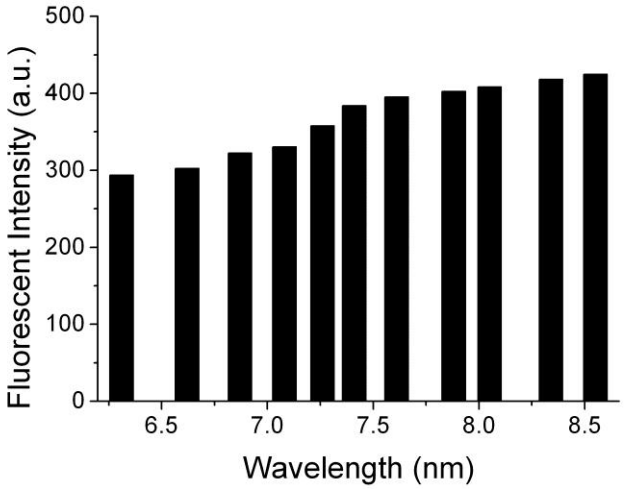


Figure S7. Fluorescent changes at 545 nm of **1** (10 μM) with 10 equiv. of Zn^{2+} between pH 6 and 8 in DMSO-HEPES (9:1, v/v).

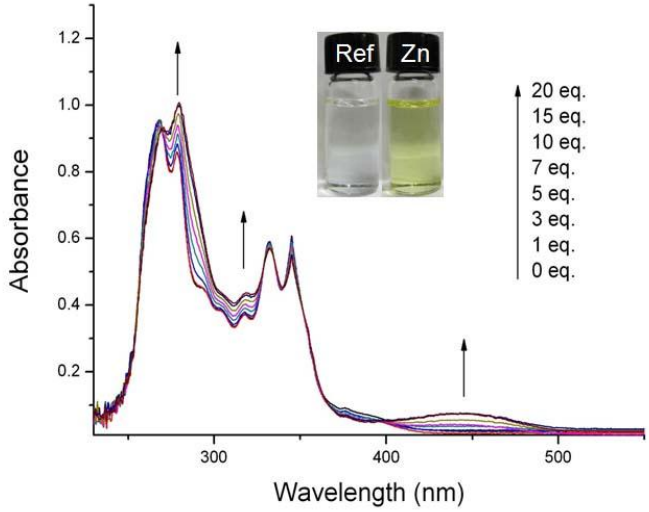


Figure S8. Absorbance titrations of **1** (10 μM) with Zn^{2+} in DMSO-HEPES buffer(0.02 M, pH= 7.4) (9:1, v/v).(inside: digital photographs of the **1** solution (10 μM) in the presence of Zn^{2+} (100 μM). Solvent: DMSO-HEPES (pH 7.4, 9:1, v/v))

More details of Reference 11 (in the main text):

Gaussian 09, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009

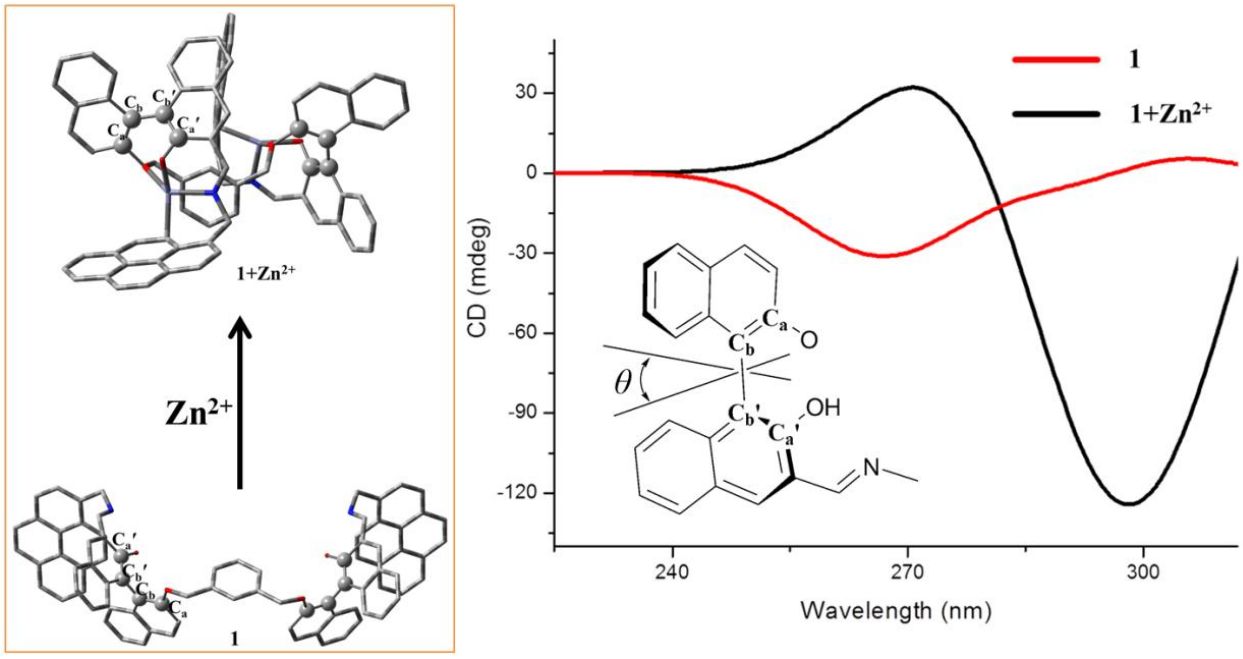


Figure S9. Calculated CD spectra as a function of the dihedral angle θ (Ca-Cb-Cb′-Ca′) of **1** and after attachment of Zn^{2+} ions.

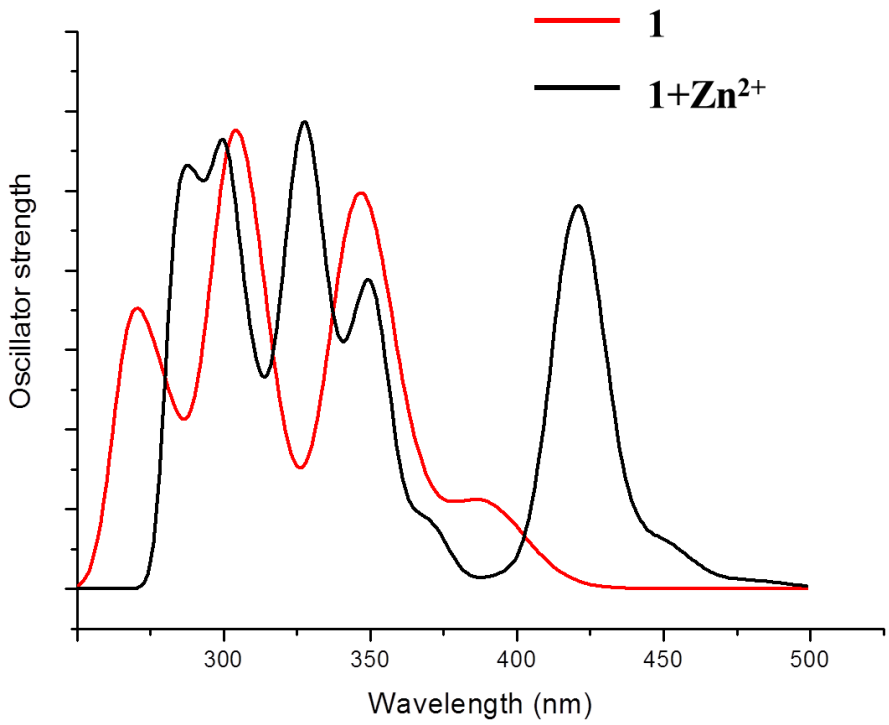
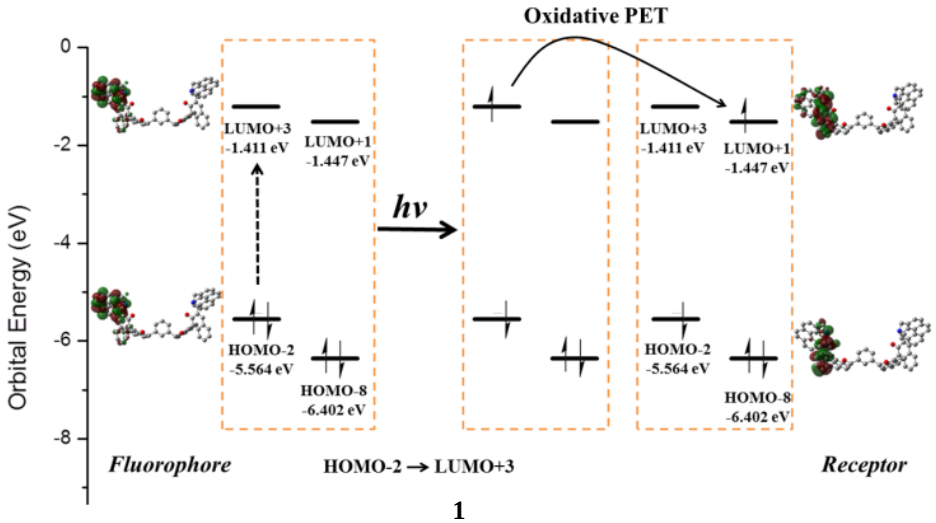


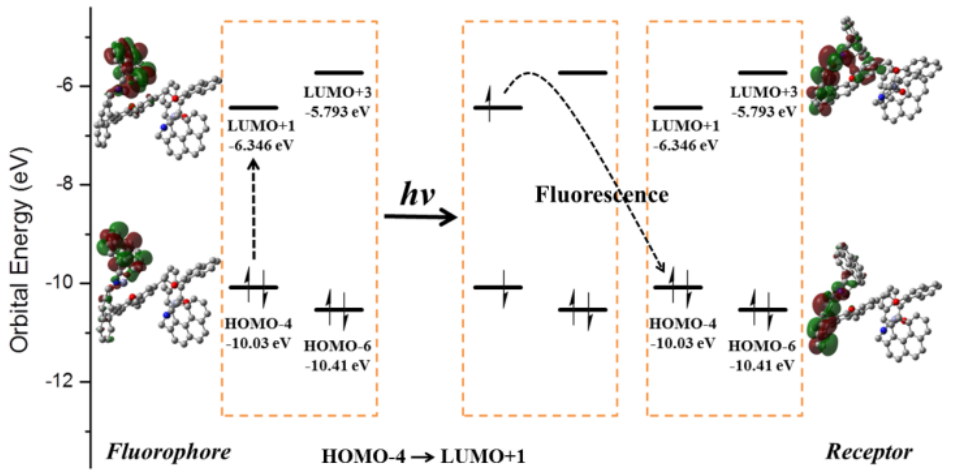
Figure S10. Simulated absorption spectra of **1** and **1**+Zn^{2+}.

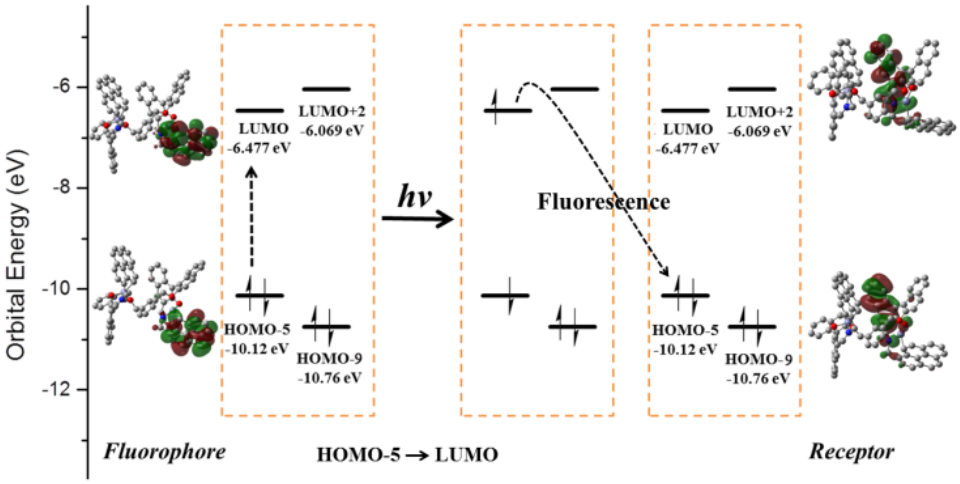
(a)


Oxidative PET
Orbital Energy (eV)
0
-2
-4
-6
-8
LUMO+3
-1.411 eV
LUMO+1
-1.447 eV
HOMO-2
-5.564 eV
HOMO-8
-6.402 eV
hv
LUMO+3
-1.411 eV
LUMO+1
-1.447 eV
HOMO-2
-5.564 eV
HOMO-8
-6.402 eV
Fluorophore
HOMO-2 → LUMO+3
Receptor

1

(b)


Orbital Energy (eV)
-6
-8
-10
-12
LUMO+1
-6.346 eV
LUMO+3
-5.793 eV
HOMO-4
-10.03 eV
HOMO-6
-10.41 eV
hv
Fluorescence
LUMO+1
-6.346 eV
LUMO+3
-5.793 eV
HOMO-4
-10.03 eV
HOMO-6
-10.41 eV
Fluorophore
HOMO-4 → LUMO+1
Receptor


Orbital Energy (eV)
-6
-8
-10
-12
LUMO
-6.477 eV
LUMO+2
-6.069 eV
HOMO-5
-10.12 eV
HOMO-9
-10.76 eV
hv
Fluorescence
LUMO
-6.477 eV
LUMO+2
-6.069 eV
HOMO-5
-10.12 eV
HOMO-9
-10.76 eV
Fluorophore
HOMO-5 → LUMO
Receptor

1+(Zn^{2+})$_2$

Figure S11. Calculated frontier orbital energy diagrams and electron transfer processes in **1** (a) and **1+(Zn^{2+})$_2$** (b) induced by light absorption