Supplementary Information for ***Acta Phys. -Chim. Sin.*** **2012**, *28* (10), 2471-2479
doi: 10.3866/PKU.WHXB201205155

新型螺吡喃衍生物：离子传感和分子水平的信息处理

李颖若[1]　张洪涛[2]　齐传民[1,*]　郭雪峰[2,3,*]

([1]北京师范大学化学学院, 放射性药物教育部重点实验室, 北京 100875; [2]北京大学化学与分子工程学院, 北京分子科学国家实验室, 分子动态与稳态结构国家重点实验室, 北京 100871; [3]北京大学工学院先进材料与纳米技术系, 北京 100871)

New Spiropyran Derivatives: Ion Sensing and Information Processing at the Molecular Level

LI Ying-Ruo[1]　ZHANG Hong-Tao[2]　QI Chuan-Min[1,*]　GUO Xue-Feng[2,3,*]

([1]*Key Laboratory of Radiopharmaceuticals, College of Chemistry, Beijing Normal University, Beijing 100875, P. R. China;* [2]*Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China;* [3]*Department of Advanced Materials and Nanotechnology, College of Engineering, Peking University, Beijing 100871, P. R. China*)

*Corresponding authors. GUO Xue-Feng, Email: guoxf@pku.edu.cn.
QI Chuan-Min, Email: qichuanmin@bnu.edu.cn.

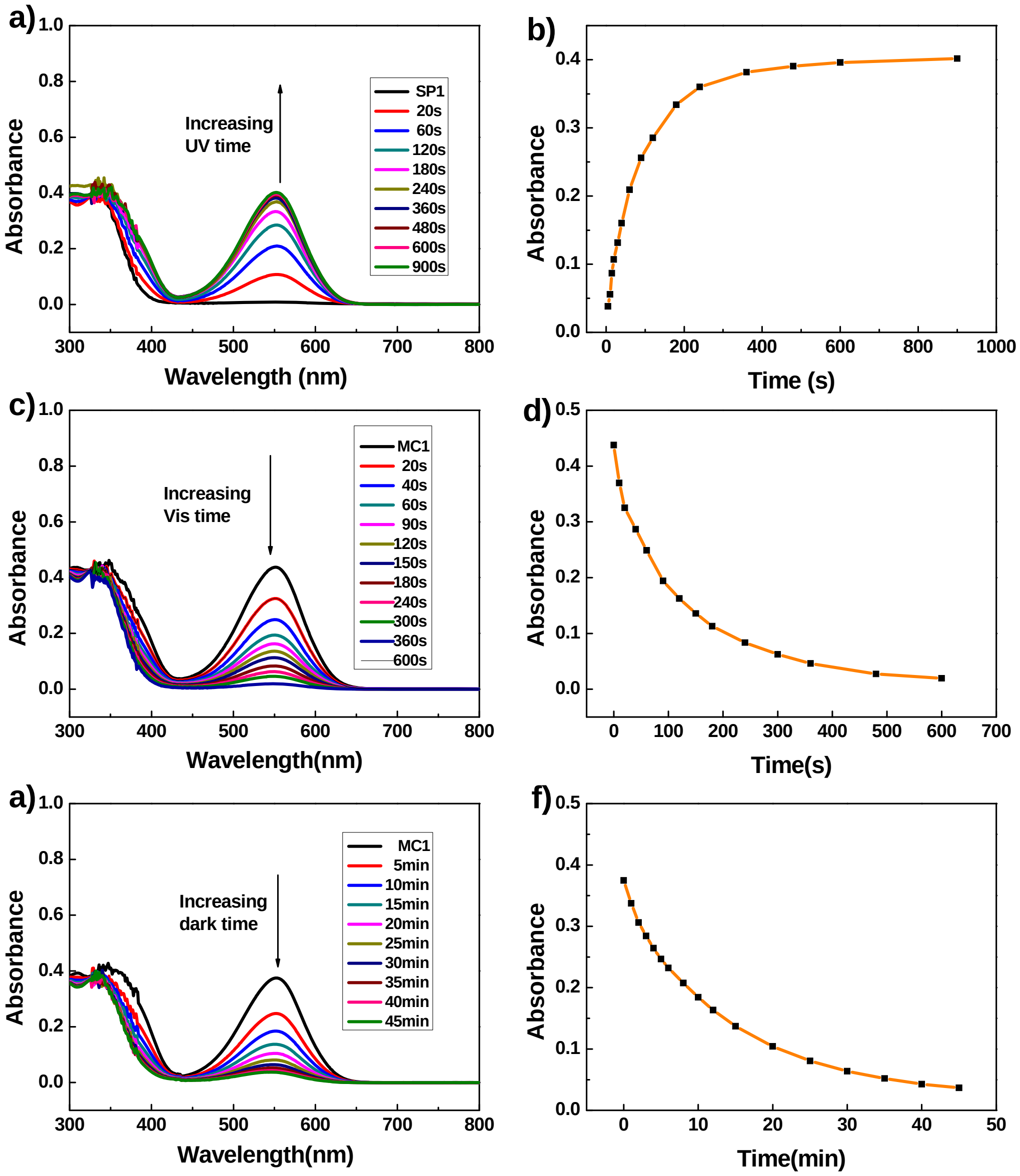

Figure S1. Evolution of the absorption spectrum a) and time dependence of the absorbance at 552 nm b) of a solution (5.0×10^{-5} M, ethanol, 293 K) of **SP1** upon UV irradiation; Evolution of the absorption spectrum c) and time dependence of the absorbance at 552 nm d) of a solution (5.0×10^{-5} M, ethanol, 293 K) of **SP1**/**MC1** upon visible irradiation after irradiation with UV light for 10 min; Evolution of the absorption spectrum e) and time dependence of the absorbance at 552 nm f) of a solution (5.0×10^{-5} M, ethanol, 293 K) of **SP1**/**MC1** in the dark after irradiation with UV light for 10 min.

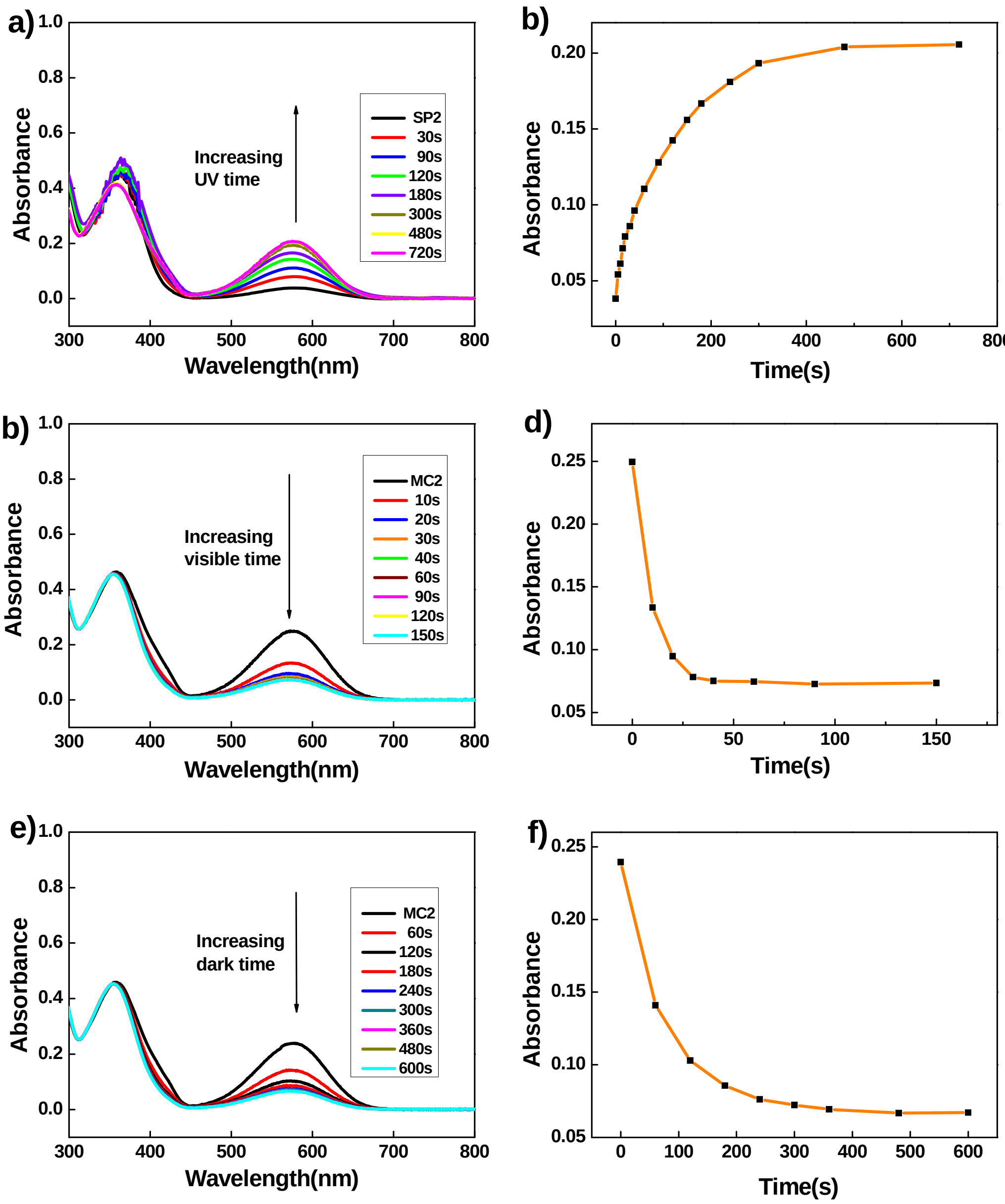

Figure S2. Evolution of the absorption spectrum a) and time dependence of the absorbance at 576 nm b) of a solution (5.0×10^{-5} M, ethanol, 293 K) of **SP2** upon UV irradiation; Evolution of the absorption spectrum c) and time dependence of the absorbance at 576 nm d) of a solution (5.0×10^{-5} M, ethanol, 293 K) of **SP2**/**MC2** upon visible irradiation after irradiation with UV light for 10 min; Evolution of the absorption spectrum e) and time dependence of the absorbance at 556 nm f) of a solution (5.0×10^{-5} M, ethanol, 293 K) of **SP2**/**MC2** in the dark after irradiation with UV light for 10 min.

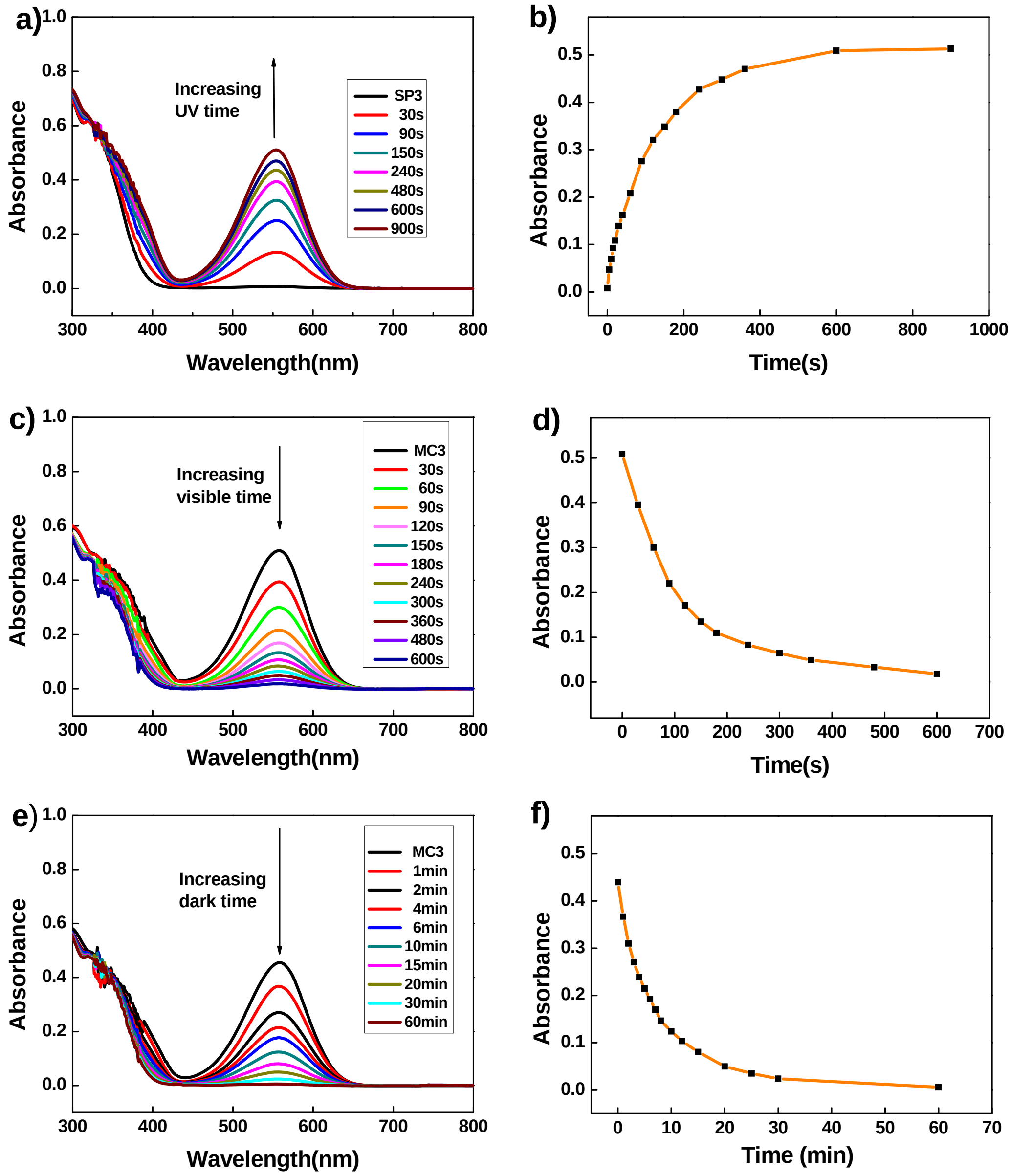

Figure S3. Evolution of the absorption spectrum a) and time dependence of the absorbance at 556 nm b) of a solution (5.0×10^{-5} M, ethanol, 293 K) of **SP3** upon UV irradiation; Evolution of the absorption spectrum c) and time dependence of the absorbance at 556 nm d) of a solution (5.0×10^{-5} M, ethanol, 293 K) of **SP3**/**MC3** upon visible irradiation after irradiation with UV light for 10 min; Evolution of the absorption spectrum e) and time dependence of the absorbance at 556 nm f) of a solution (5.0×10^{-5} M, ethanol, 293 K) of **SP3**/**MC3** in the dark after irradiation with UV light for 10 min.

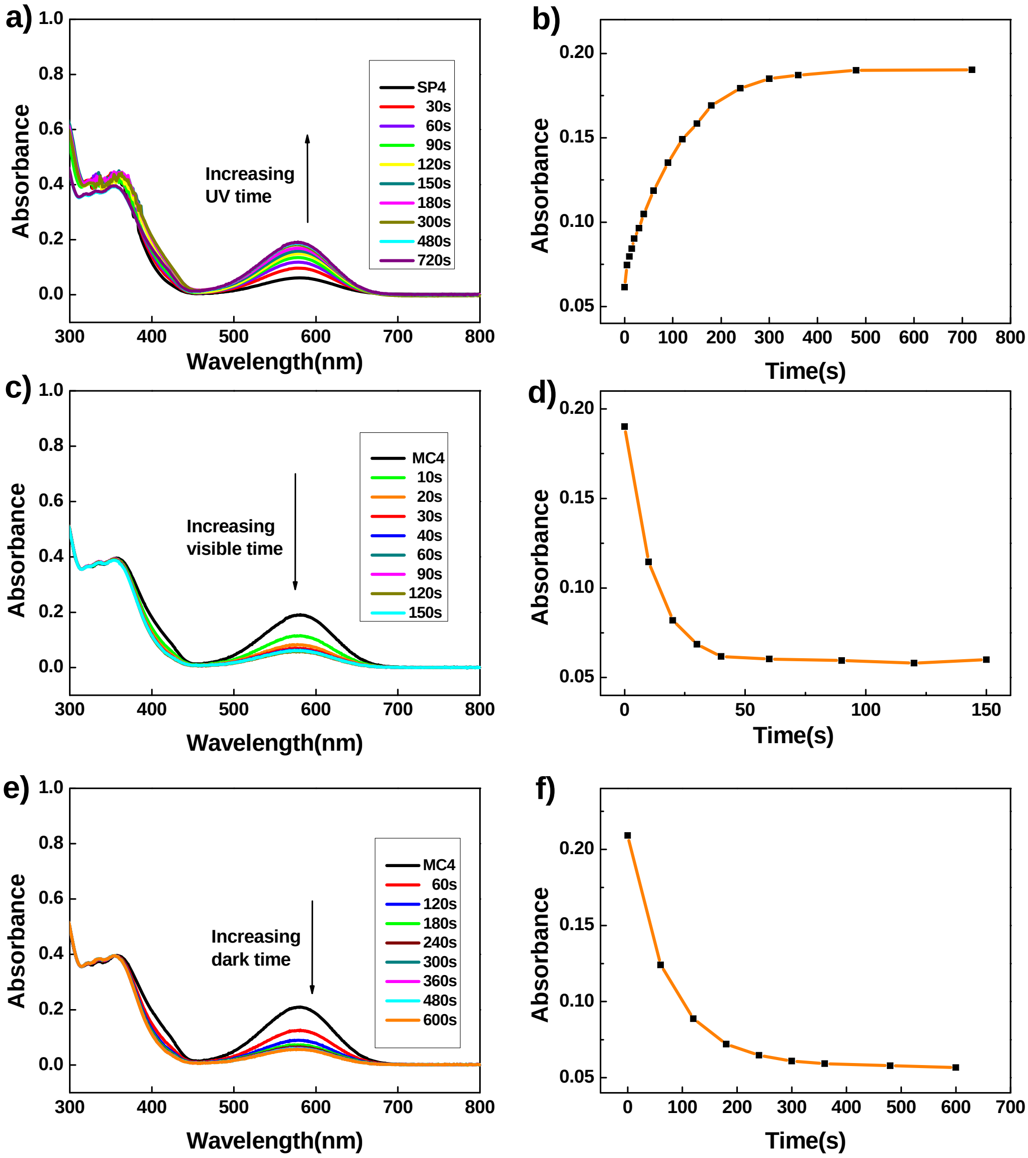

Figure S4. Evolution of the absorption spectrum a) and time dependence of the absorbance at 583 nm b) of a solution (5.0×10^{-5} M, ethanol, 293 K) of **SP4** upon UV irradiation; Evolution of the absorption spectrum c) and time dependence of the absorbance at 583 nm d) of a solution (5.0×10^{-5}M, ethanol, 293 K) of **SP4**/**MC4** upon visible irradiation after irradiation with UV light for 10 min; Evolution of the absorption spectrum e) and time dependence of the absorbance at 583 nm f) of a solution (5.0×10^{-5} M, ethanol, 293 K) of **SP4**/**MC4** in the dark after irradiation with UV light for 10 min.

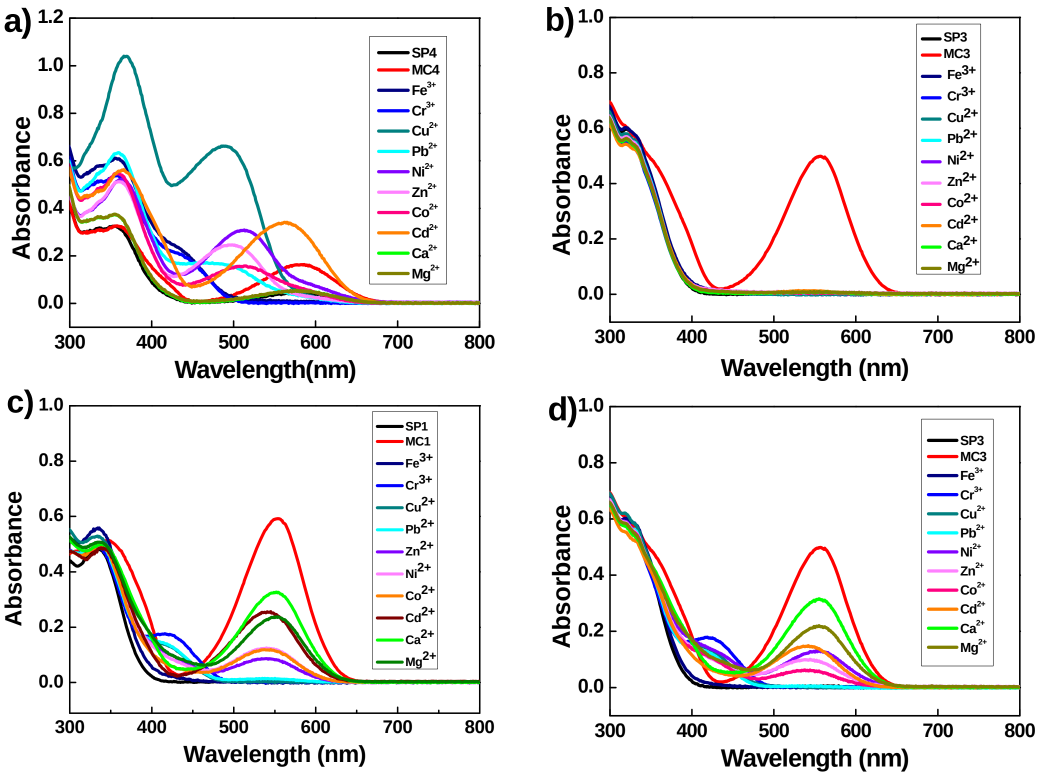

Figure S5. Absorption spectra of **SP4** (5.0×10^{-5} M, ethanol, 293 K) after addition of 1 equiv. of different metal ions stored in the dark a); Absorption spectra of **SP3** (5.0×10^{-5} M, ethanol, 293 K) after addition of 1 equiv. of different metal ions stored in the dark b); Absorption spectra of **SP1** (5.0×10^{-5} M, ethanol, 293 K) after addition of 1 equiv. of different metal ions further irradiated with UV light for 5 min c); Absorption spectra of **SP3** (5.0×10^{-5} M, ethanol, 293 K) after addition of 1 equiv. of different metal ions further irradiated with UV light for 5 min d).

Table S1. Summary of the maximum absorption wavelength (λ_{max}) of **SP1** and **SP2** in ethanol solution in the absence the presence of different metal ions and corresponding changes of the maximum absorption wavelength ($_{\Delta}\lambda_{max}$)

Metal ions	SP3		SP4	
	λ_{max} (nm)	$_{\Delta}\lambda_{max}$ (nm)	λ_{max} (nm)	$_{\Delta}\lambda_{max}$ (nm)
none	556		583	
Fe^{3+}	~420	>100	~420	>100
Cr^{3+}	~420	>100	~420	>100
Pb^{2+}	~420	>100	480	>100
Cu^{2+}	~420	>100	490	93
Cd^{2+}	538	18	560	23
Co^{2+}	540	16	520	63
Zn^{2+}	541	15	504	79
Ni^{2+}	541	15	516	67
Ca^{2+}	556	0	566	17
Mg^{2+}	556	0	574	9

Table S2. Summary of some important parameters of the metal ions

Metal ions	coordination number	ionic radius (pm)	ionic electro-negativity	electron configuration
none				
Fe^{3+}	6	65	1.83	$[Ar]3d^5$
Cr^{3+}	6	62	1.66	$[Ar]3d^3$
Pb^{2+}	4	119	1.87	$[Xe]6s^26p^2$
Cu^{2+}	4,6	73	1.9	$[Ar]3d^9$
Cd^{2+}	4,6	97	1.69	$[Kr]4d^{10}$
Co^{2+}	6	75	1.88	$[Ar]3d^7$
Zn^{2+}	4,6	74	1.65	$[Ar]3d^{10}$
Ni^{2+}	6	70	1.91	$[Ar]3d^8$
Ca^{2+}	6,8	99	1.01	$[Ar]4s^2$
Mg^{2+}	4,6	72	1.31	$[Ne]3s^2$

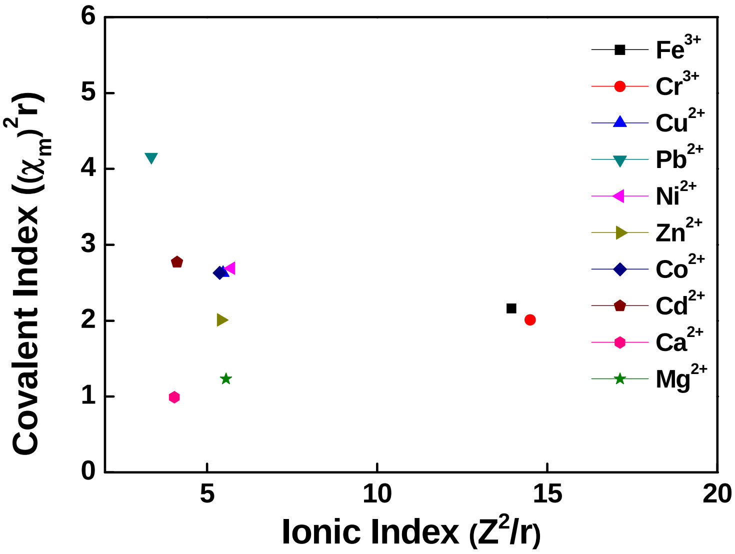

Figure S6. Abbreviated Nieboer and Richardson metal ion classification scheme. For each of the metal ions, the Class B or covalent-bonding index $(\chi_m)^2r$ is plotted against the class A or ionic index, Z^2/r. In these expressions, Z is the ion charge, χ_m is the metal-ion Pauling electronegativity and r is the ionic radius corresponding to the most common coordination number.

Nieboer and Richardson suggested back in 1980 that important environmental metals can be categorized into three classes, Class A, Class B and Intermediate Class, and that this classification system might be particularly applicable for use in research on aspects of environmental pollution. This classification scheme allows the prediction of certain spectroscopic properties related to the interaction of various metal ions with substances. Figure S6 presents portion of the Nieboer and Richardson classification scheme. In this classification metal ions are separated into three categories: Class A (oxygen-seeking, ‘hard’ acids), Class B (nitrogen/sulfur seeking, ‘soft’ acids) and Borderline (intermediate or ambivalent). Accordingly, the metal ions we studied can be classified using this method (Elkins, K. M.; Nelson, D. J., *Coord. Chem. Rev.* **2002**, *228*, 205) and the change of the spectra have some relationship with the location of the metal ions in the scheme. This also indicate the metal ion impact the properties of the complex tremendously.

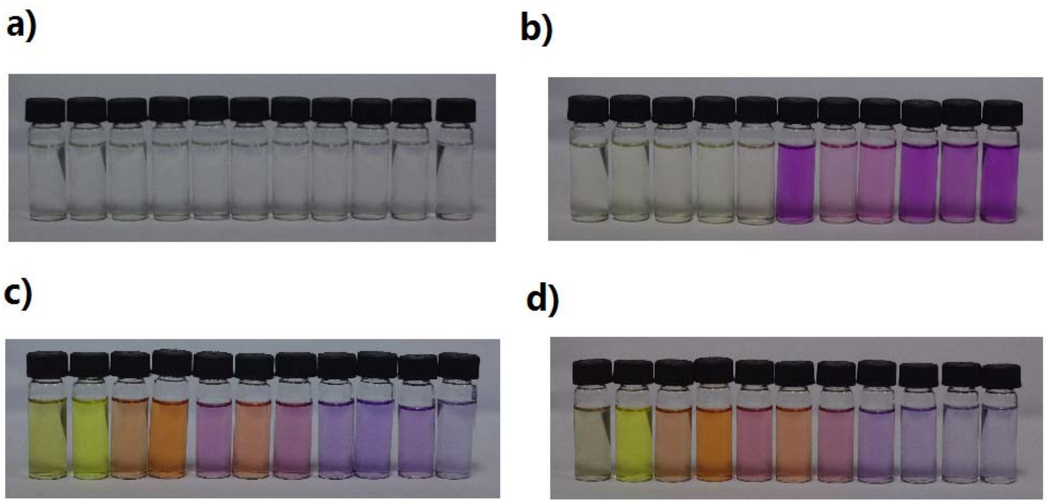

Figure S7. Photographs of solutions of **SP1** (5×10^{-5} M) in absence and presence of 1 equiv. of different metal ions in ethanol before a) and after UV irradiation b); Photographs of solutions of **SP2** (5×10^{-5} M) c) and **SP4** (5×10^{-5} M) d) in absence and presence of 1 equiv. of different metal ions in ethanol. The vials in each group were added with Fe^{3+}, Cr^{3+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+},Co^{2+}, Cd^{2+}, Ca^{2+}, Mg^{2+} and blank from left to right.

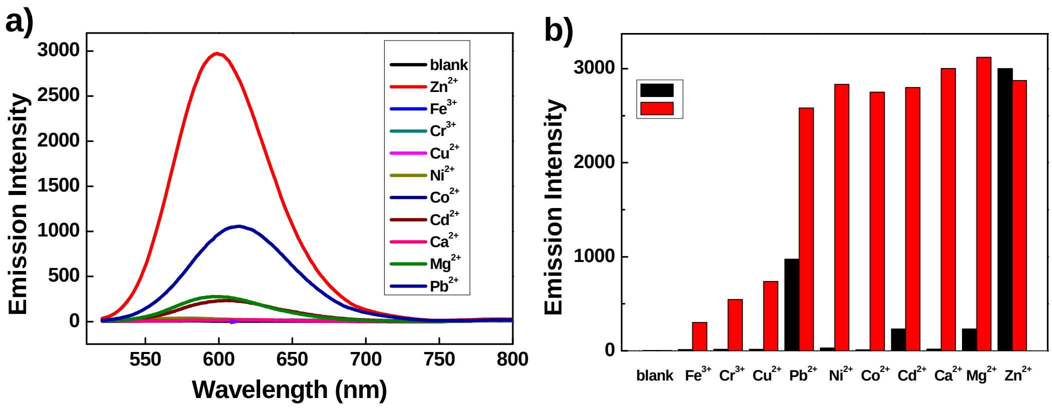

Figure S8. a) Fluorescence emission spectra (λ_{ex} = 497 nm) of **SP4** (5.0×10^{-5} M, ethanol, 293 K) upon additions of 1 equiv. of metal ions (Zn^{2+}, Fe^{3+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Co^{+}, Cd^{2+}, Ca^{2+}, Mg^{2+} and Pb^{2+}); b) Metal ion selectivity profiles of **SP4** (5.0×10^{-5} M, ethanol, 293 K) in the presence of various metal ions (λ_{ex} = 497 nm): (black bars) fluorescence emission intensity at 600 nm in the presence of 1 equiv. of Fe^{3+}, Cr^{3+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+} , Ca^{2+}, Mg^{2+} and Zn^{2+}; (red bars) fluorescence emission intensity at 600 nm after further addition of 1 equiv. of Zn^{2+}.

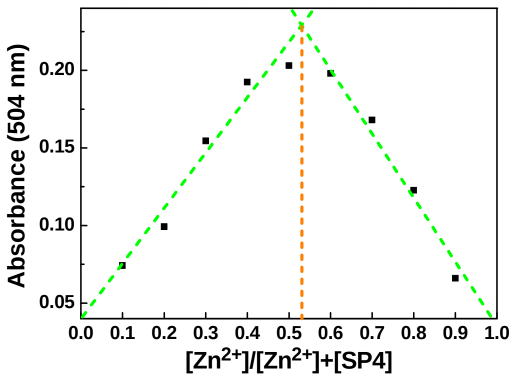

Figure S9. Job's plot of **SP4** with Zn^{2+} in ethanol solution. Total concentration of [**SP4**] + **[**Zn^{2+}**]** was kept constant at 5×10^{-5} M. The absorbance at 504 nm was used.

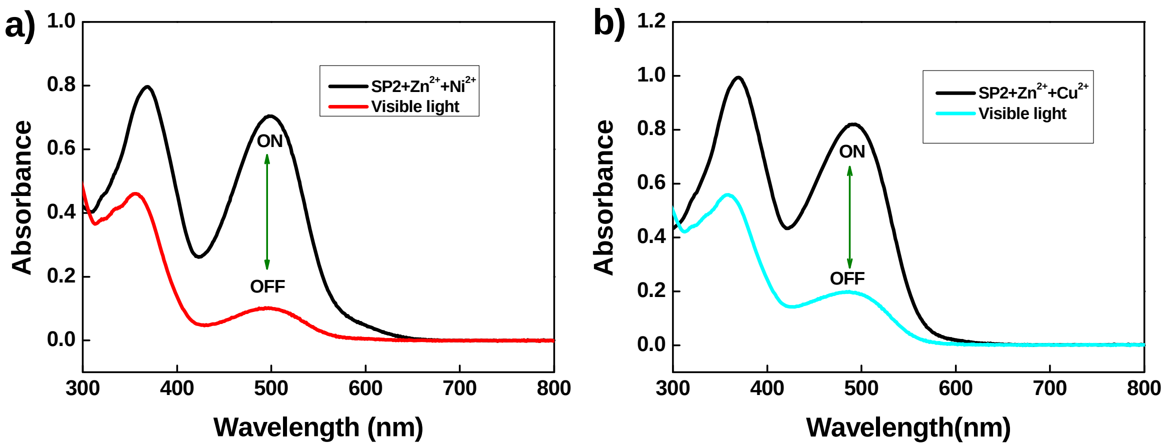

Figure S10. The absorption spectra of **SP2** in presence of 1equiv of Zn^{2+} and 1 equiv. of Ni^{2+} or Cu^{2+} .