Electronic Supplementary Material (ESI) for Chemical Communications

A pyridinyl-functionalized tetraphenylethylene fluorogen for specifically sensing trivalent cations

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Experimental Section

Materials: Diphenylether and 4-bromobenzophenone were purchased from Alfa Aesar. *n*-BuLi was purchased from Acros. Trifluoroacetic acid (TFA) was purchased from Aladdin. Palladium (II) acetate [$Pd(OAc)_2$] was purchased from Aldrich and used as received without further purification. Other reagents including *p*-toluene-sulfonic acid (TsOH), triphenylphosphine, toluene, *n*-hexane, ethanol, copper (II) chloride, iron(II) sulfate heptahydrate, ferric chloride, zinc chloride, silver nitrate, chromium chloride, nickel(II) chloride, magnesium sulfate, sodium chloride, calcium chloride, cadmium chloride, aluminum sulfate, lead nitrate, and mercuric nitrate were purchased from Sinopharm Chemical Reagent Co., Ltd. Tetrahydrofuran (THF) was distilled under normal pressure from sodium benzophenone ketyl under nitrogen immediately prior to use.

Instrumentation: ^1H and ^{13}C NMR spectra were measured on a Mercury plus 400MHz NMR spectrometer in $CDCl_3$ or DMSO-d_6 using tetramethylsilane (TMS; δ = 0 ppm) as internal standard. High-resolution mass spectra (HRMS) were taken on a GCT premier CAB048 mass spectrometer operating in a MALDI-TOF mode. Elemental analysis was performed on a ThermoFinnigan Flash EA1112 apparatus. FL spectra were recorded on a Hitachi 4500 spectrofluorometer. UV-vis absorption spectra were obtained on a Milton Ray Spectrofluorometer.

Synthesis of ***(E)-4-(4-(1,2,2-triphenylvinyl)styryl)pyridine (Py-TPE)***: TPE-containing precursor 1,1,2-triphenyl-2(4′-bromophenyl)ethene (**3**) was synthesized according to our previously published paper.[1] A mixture of 2.056 g (5.0 mmol) of **3**, 56 mg (0.25 mmol) of $Pd(OAc)_2$ and 0.157 g (0.6 mmol) of $P(C_6H_5)_3$ was placed in a N_2-purged Schlenk tube. After adding 0.8 mL (7.5 mmol) of 4-vinylpyridine and 3 mL dry Et_3N, the tube was sealed. The mixture was heated to 100 ^oC in an oil bath and stirred for 3 days at this temperature. After being cooled to room temperature, the resultant was dissolved in DCM and extracted with water for three times. After filtration and solvent evaporation, the crude product was purified on a silica-gel column using hexane/THF (2/1 v/v) as eluent. A yellow solid was obtained in 63.6% yield. In Figure S1, In Figure S1, ^1H NMR (400 MHz, DMSO-d_6), δ (TMS, ppm): 8.52 (d, 2H, pyridine-**H**), 7.51 (d, 2H, pyridine-**H**), 7.46-7.40 (m, 3H, CH=C**H** &Ph-**H**), 7.21-6.98 (m, 18H, Ph-**H**). In Figure S2, ^1H NMR (400MHz, $CDCl_3$), δ (TMS, ppm): 8.53 (d, 2H, pyridine-**H**), 7.28 (d, 2H, pyridine-**H**), 7.17 (d, 1H, CH=C**H**), 6.85 (d, 1H, CH=C**H**), 7.14-7.02 (m, 19H, Ph-**H**). ^{13}C NMR (400 MHz, CDCl3), δ (TMS, ppm): 150.08, 144.60, 144.42, 143.52, 143.47, 143.39, 141.51, 140.26, 134.04, 132.81, 131.78, 131.29, 131.26, 131.23, 127.73, 127.69, 127.60, 126.56, 126.53, 126.49, 126.32, 125.53, 120.65. In Figure S3, HRMS (MALDI-TOF, *m*/*z*): [M^+] calcd for $C_{33}H_{25}N$, 435.1987; found 435.1967. Elemental analysis: calcd (%): C, 91.00; H, 5.79; N, 3.22; found (%): C, 90.57; H, 6.04; N, 2.96.

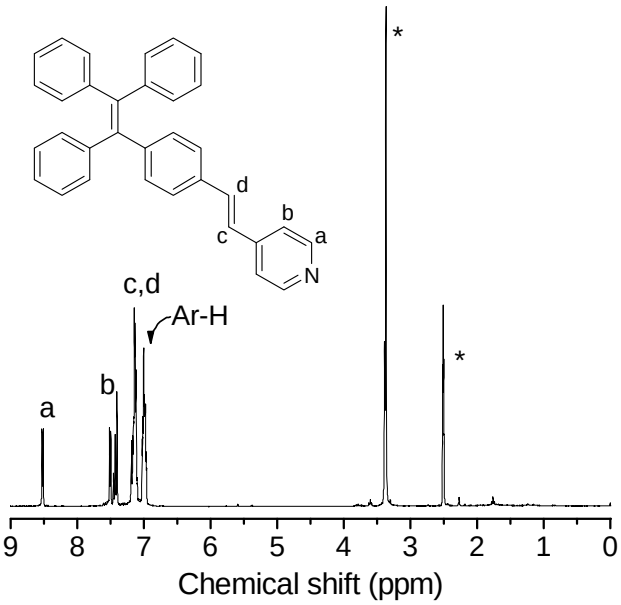

Fig. S1 ^{1}H NMR spectrum of Py-TPE in DMSO-d_6. The solvent peaks are marked with asterisks.

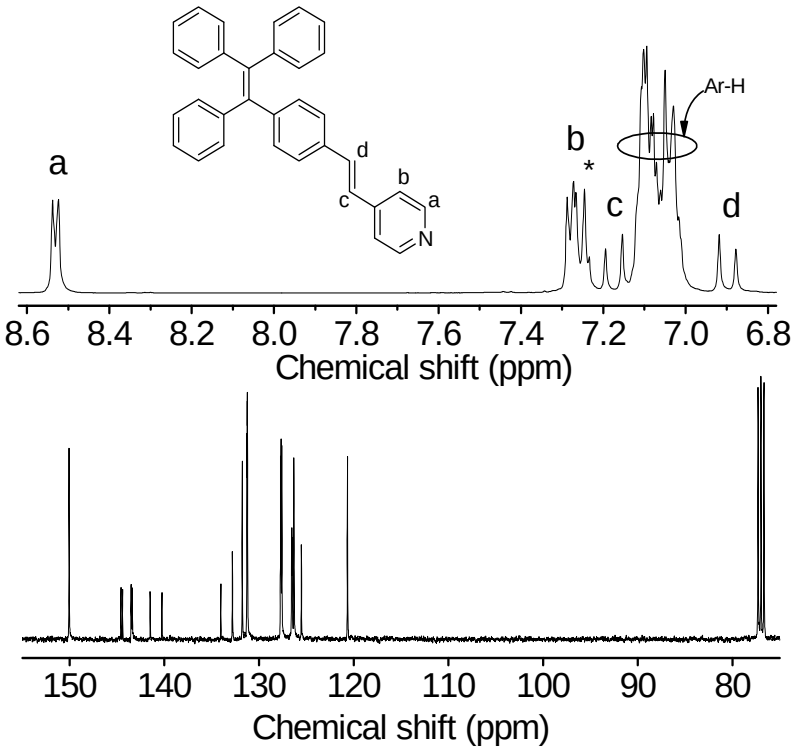

Fig. S2 ^{1}H NMR and ^{13}C NMR spectra of Py-TPE in $CDCl_3$. The solvent peak is marked with asterisks.

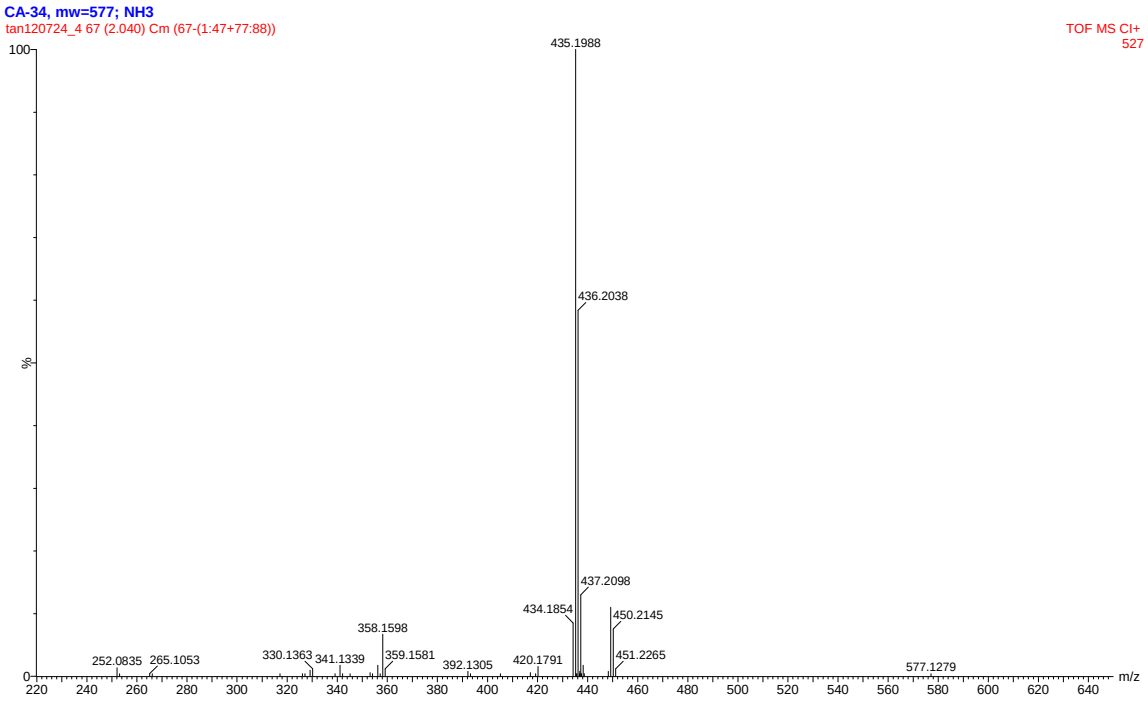

Fig. S3. HRMS spectrum of Py-TPE.

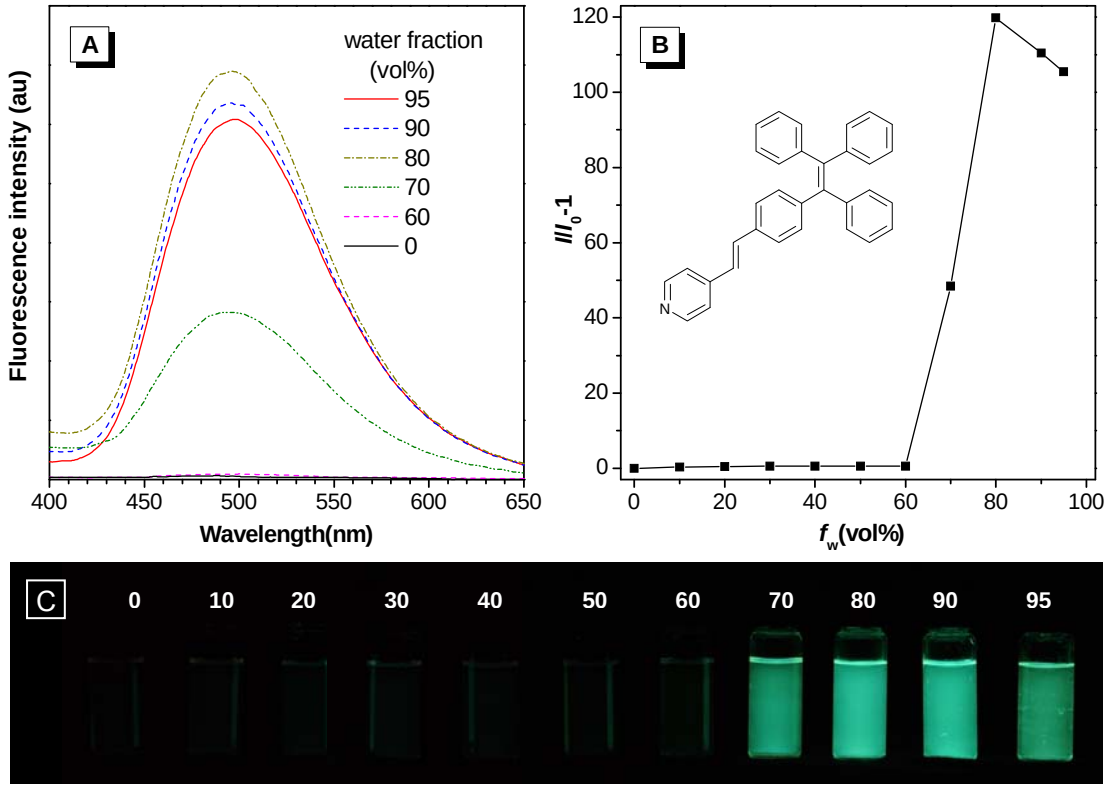

Fig. S4 (A) Fluorescence spectra of Py-TPE in ethanol/water mixture solutions with different water fraction (f_w, in volume percentage, vol%). (B) Plot of the changes in fluorescence intensity with f_w, where I_0 and I are the maximal fluorescence intensity recorded before and after addition water into Py-TPE ethanol solution. Inset of B is the molecular structure of Py-TPE. (C) Images of the above solutions taken under UV light. Excitation Concentration of Py-TPE ([Py-TPE]) = 10 μM, excitation wavelength (λ_{ex}) for all experiments = 365 nm.

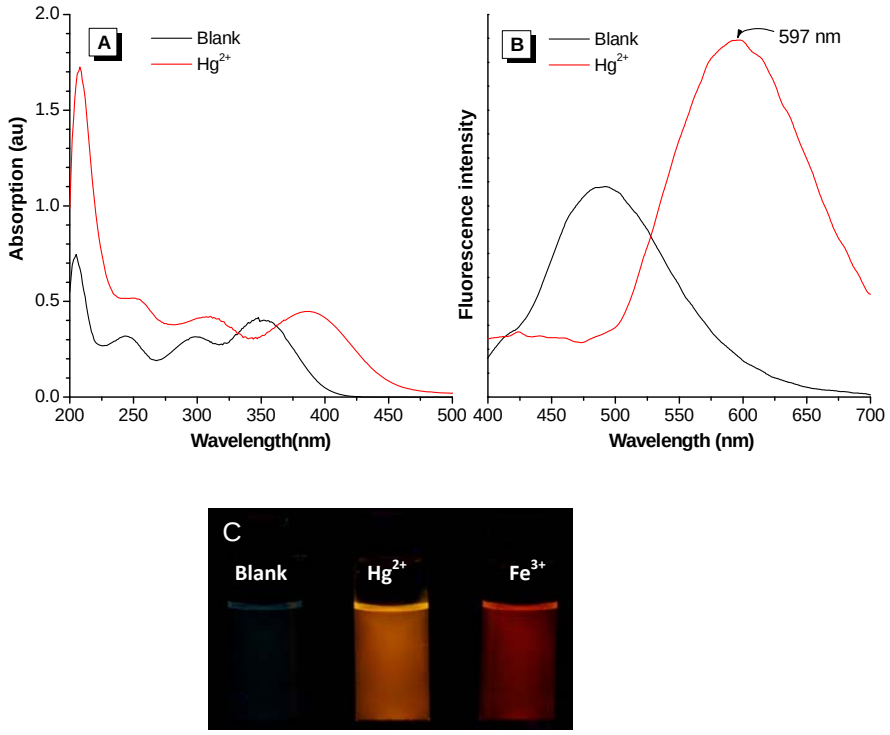

Fig. S5 (A) Absorption and (B) fluorescence spectra of Py-TPE in ethanol (containing 0.5% water) with different concentration of Hg^{2+}. The absorption and fluorescence spectra of the blank sample are also shown in (A) and (B) for comparison. (C) Fluorescence images of the above solutions taken under UV light. λ_{ex}: 365nm. Concentration of Py-TPE: 10 μM. The red emission image of the mixtures of Py-TPE and Fe^{3+} in ethanol/water solution is also shown as a reference.

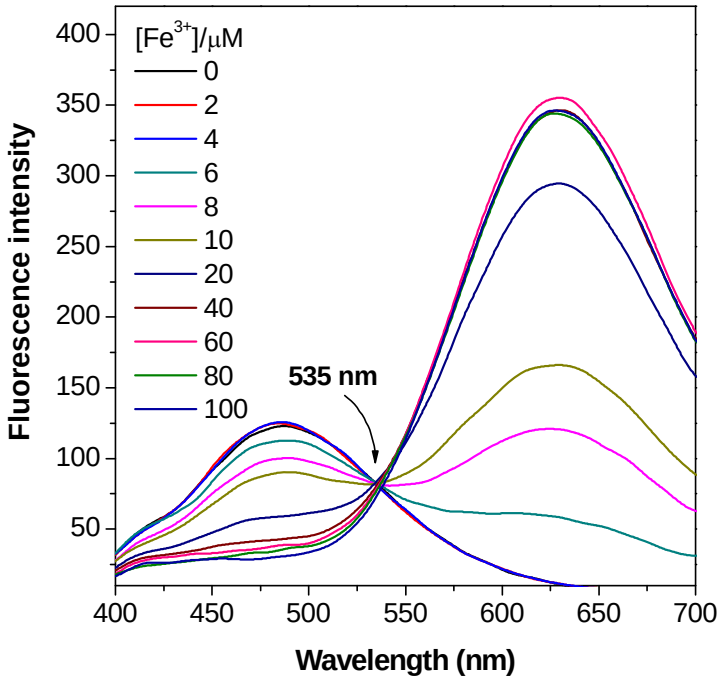

Fig. S6 Fluorescence spectra of Py-TPE in ethanol (containing 0.5% water) with different concentration of Fe^{3+} ($[Fe^{3+}]$ = 0, 2, 4, 6, 8, 10, 20, 40, 60, 80, 100 μM). λ_{ex}: 365nm. Concentration of Py-TPE: 10 μM.

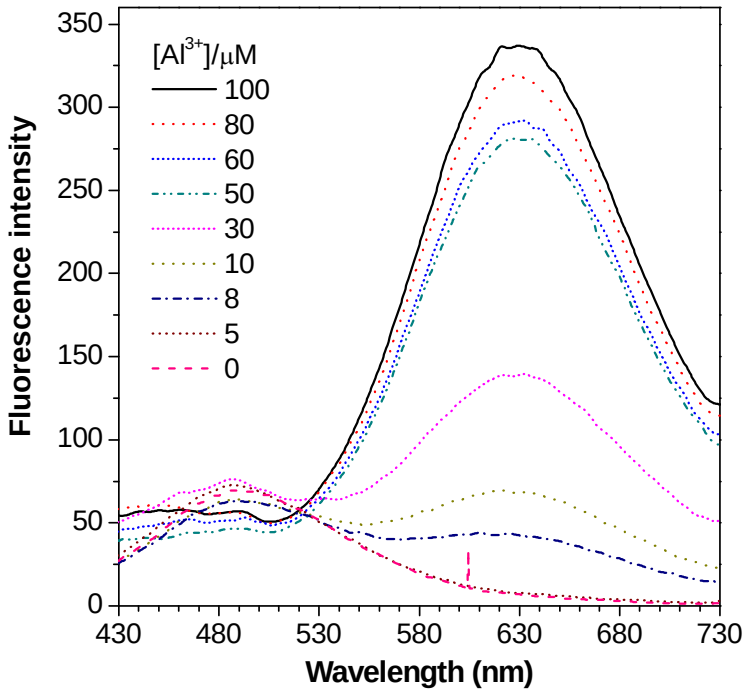

Fig. S7 Fluorescence spectra of Py-TPE in ethanol (containing 0.5% water) with different concentration of Al^{3+} ($[Al^{3+}]$ = 0, 5, 8, 10, 30, 50, 60, 80, 100 μM). λ_{ex}: 365nm. Concentration of Py-TPE: 10 μM..

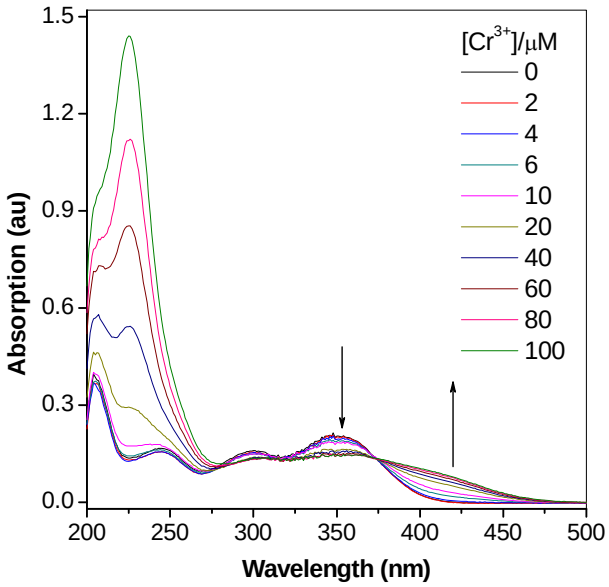

Fig. S8 Absorption spectra of Py-TPE in ethanol solution and the mixtures of Py-TPE and Cr^{3+} in ethanol/water solutions with different concentration of Cr^{3+}. Concentration of Py-TPE: 10 μM.

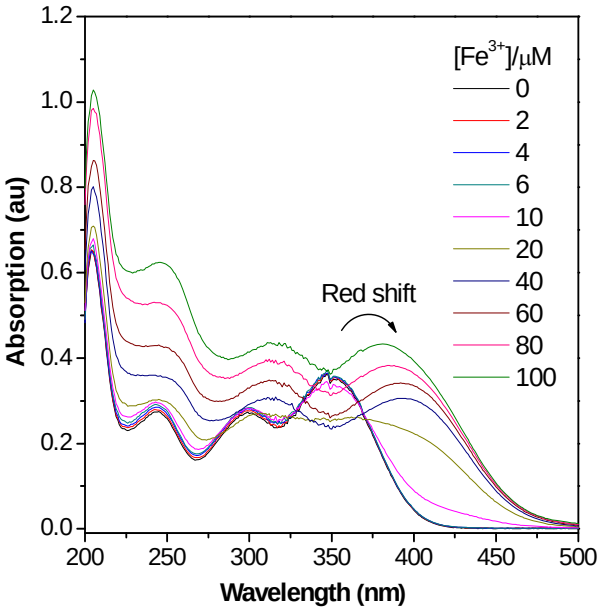

Fig. S9 Absorption spectra of Py-TPE in ethanol solution and the mixtures of Py-TPE and Fe^{3+} in ethanol/water solutions with different concentration of Fe^{3+}. Concentration of Py-TPE: 10 μM.

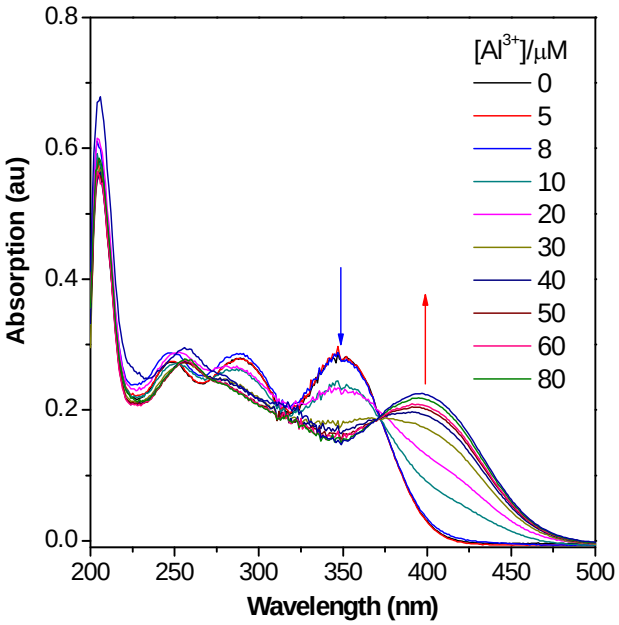

Fig. S10 Absorption spectra of Py-TPE in ethanol solution and the mixtures of Py-TPE and Al^{3+} in ethanol/water solutions with different concentration of Al^{3+}. Concentration of Py-TPE: 10 μM.

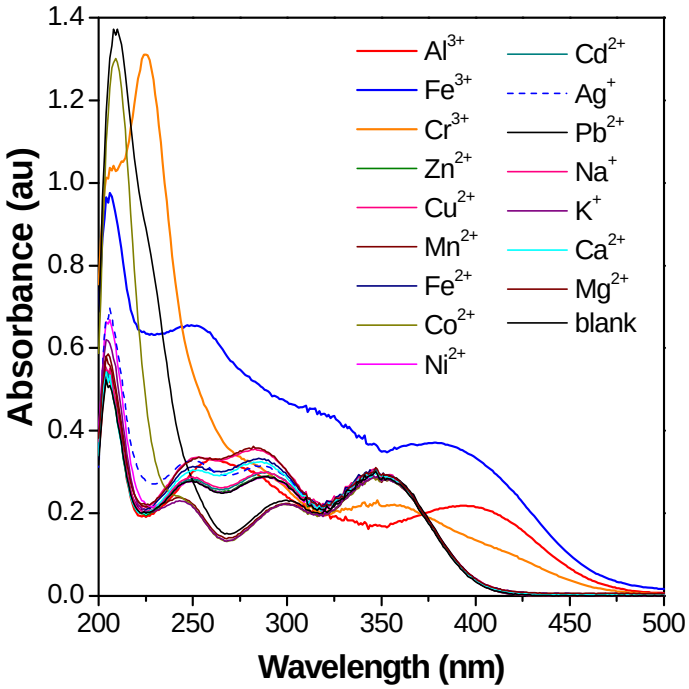

Fig. S11 Absorption spectra of Py-TPE in ethanol solution and the mixtures of Py-TPE and different metal cations in ethanol/water solutions. Concentration of Py-TPE: 10 μM, concentration of metal cations: 10 μM.

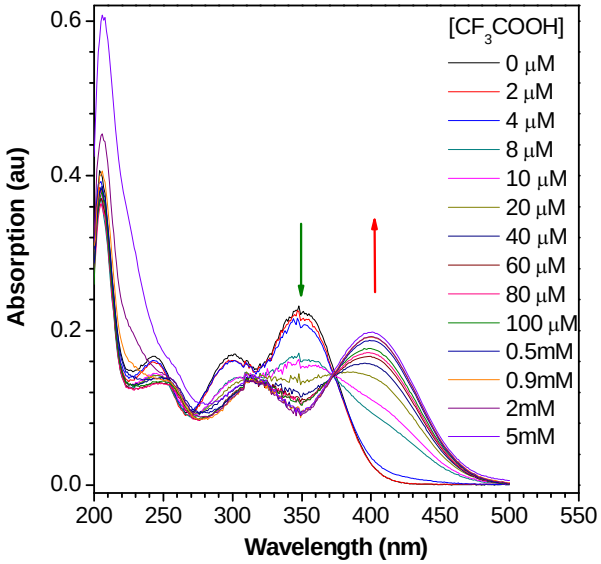

Fig. S12 Absorption spectra of Py-TPE and protonated Py-TPE ethanol/water solutions with different concentration of trifluoroacetic acid. Concentration of Py-TPE: 10 μM.

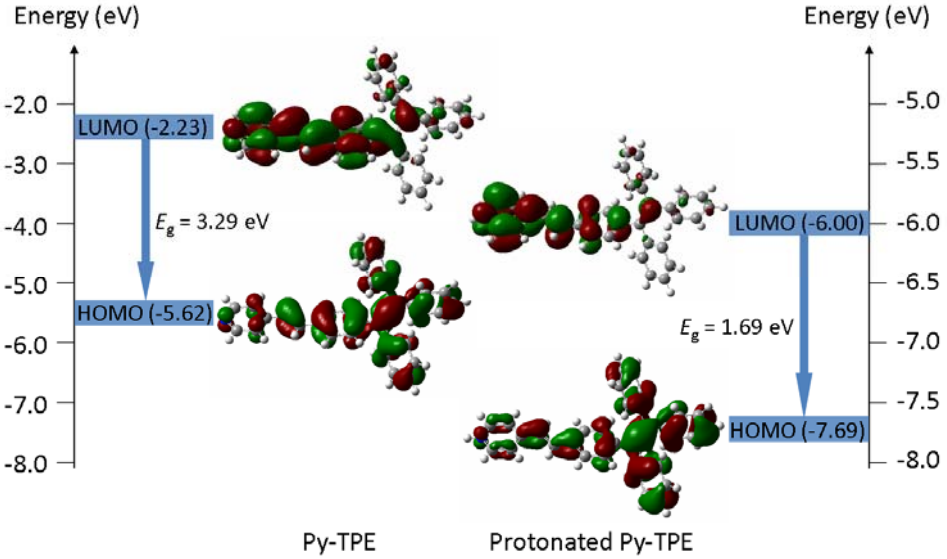

Fig. S13. Frontier molecular orbital plots and energy level diagrams of Py-TPE and protonated Py-TPE. The calculations were performed using B3LYP/6-31+G(D) as implemented on Gaussian09.[2]

References

1. Y. Liu, C. Deng, L. Tang, A. Qin, R. Hu, J. Z. Sun and B. Z. Tang, *J. Am. Chem. Soc*., 2011, 133, 660.

2. Gaussian 09 (Revision A.02), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, Jr, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowskiand D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.