Supplementary Material (ESI) for New Journal of Chemistry

Electronic Supplementary Information

Tetrathiafulvalene Derivatives bearing Crown Ether with Intramolecular Charge Transfer Properties: Synthesis, Cations Binding Studies

Yao-Peng Zhao, Xiao-Jun Wang, Jing-Jing Wang, Gang Si, Yan Liu, Chen-Ho Tung and Li-Zhu Wu*

Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, the Chinese Academy of Sciences, Beijing 100190, P. R. China.

E-mail: lzwu@mail.ipc.ac.cn

General

All reagents were obtained from commercial sources and used as received unless otherwise noted. Reactions requiring anhydrous conditions were conducted under a nitrogen or argon atmosphere. Tetrahydrofuran (THF) and triethylamine (TEA) were distilled over sodium/benzophenone ketyl and CaH_2 under a nitrogen atmosphere prior to use, respectively. 2-iodotetrathiafulvalene (I-TTF) and HC≡CR were prepared according to literature procedures[1].

UV-vis spectra were obtained on a Shimadzu UV-1601PC spectrophotometer. Elemental analyses (CHN) were performed at FLASH EA1112. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker (400 MHz, 300 MHz) spectrometers at room temperature (298K). Chemical shifts were reported versus tetramethylsilane and referenced to the residual solvent peaks. Cyclic voltammetry (CV) was performed using a Princeton Applied Research potentiostat/galvanostat model 263A. Anhydrous MeCN (Aldrich) was used as the solvent under inert atmosphere (Ar) and 0.1 M tetra(n-butyl)ammonium hexafluorophosphate ($TBAPF_6$) was used as the supporting electrolyte.

Electrochemistry

Cyclic voltammetry (CV) was performed using a Princeton Applied Research potentiostat/galvanostat model 283, in a three-electrode single-compartment cell equipped with platinum electrodes of area 0.125 cm^2, a platinum-plate counter electrode, and a SCE reference electrode. Anhydrous MeCN (Aldrich) was used as the solvent under inert atmosphere (Ar) and 0.1 M tetra(n-butyl)ammonium hexafluorophosphate (TBAPF$_6$) was used as the supporting electrolyte.

UV-vis spectra

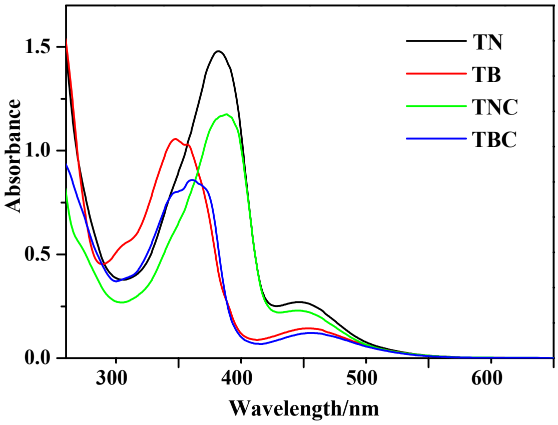


Fig. S1 Absorption spectra of **TNC**, **TBC**, **TN** and **TB** in CH_3CN solution (10^{-5} M) at room temperature.

The stoichiometry and Binding Constant Determinations

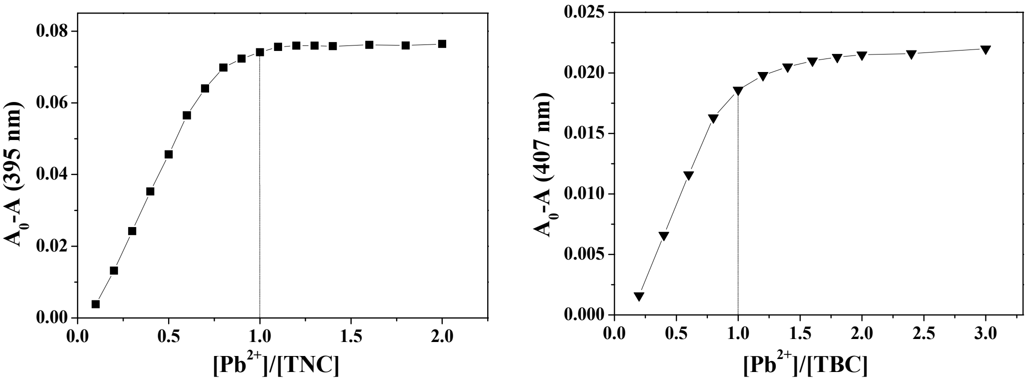
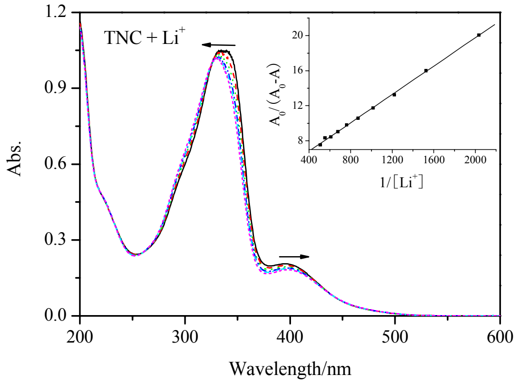


Fig. S2 Mol-ratio plots of the absorbance change at 395 and 407 nm for **TNC** and **TBC**, respectively. And the absorption bands at 395 and 407 nm linearly increased up to a 1:1 [Pb^{2+}]/[TNC or TBC] ratio, which is consistent with a 1:1 complex stoichiometry.

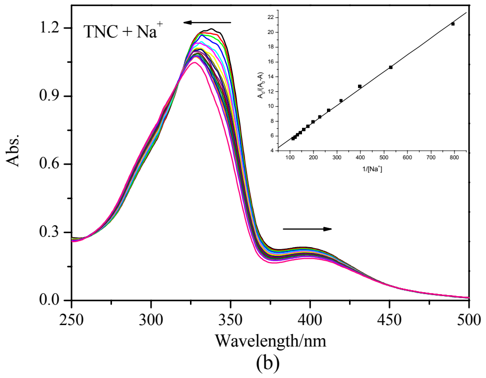
The absorption spectral titration for the determination of binding constants was performed at 298 K. The supporting electrolyte (0.1 mol/L tetrabutylammonium hexafluorophosphate) was added to maintain a constant ionic strength of the sample solution. The ion binding constants (Ks) were calculated from the following equation:[2]

$$A_0/(A_0 - A) = A_0/\alpha C_0 + (A_0/\alpha C_0 K_s)(1/[M])$$

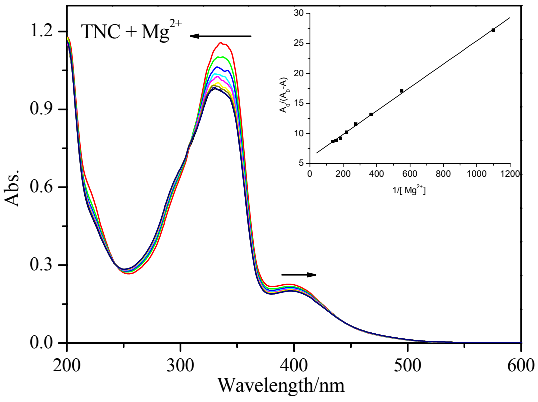
where A and A_0 are the absorbance for **TBC** and **TNC** at 407 and 395 nm in the presence and absence of metal ion, respectively; α is the ratio of the **TBC**/ **TNC** and Pb^{2+}; C_0 is the concentration of **TBC** and **TNC**; and [M] is the concentration of the Pb^{2+} ion.


TNC + Li$^+$
Abs.
1.2
0.9
0.6
0.3
0.0
200
300
400
500
600
Wavelength/nm
A$_0$/(A$_0$-A)
20
16
12
8
400
800
1200
1600
2000
1/[Li$^+$]

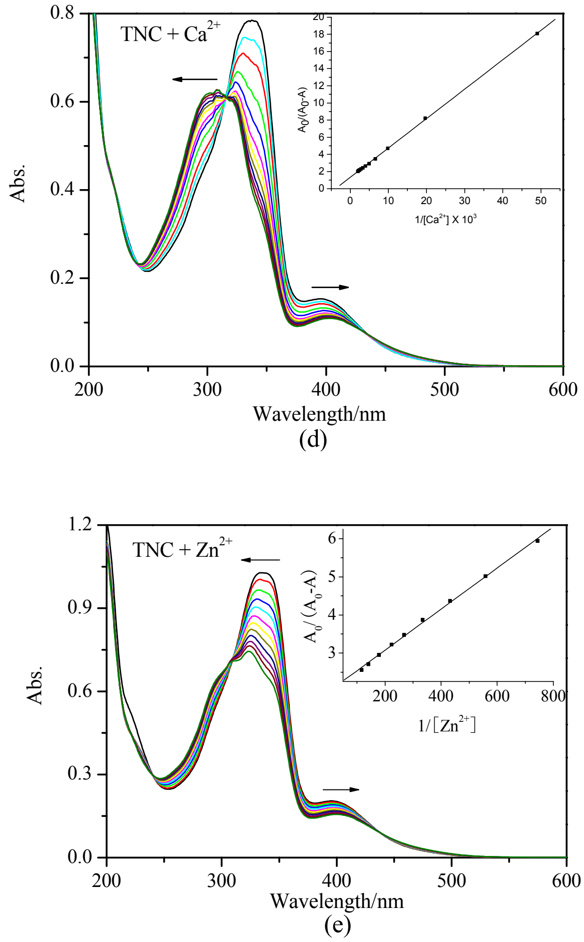
(a)


TNC + Na$^+$
Abs.
1.2
0.9
0.6
0.3
0.0
250
300
350
400
450
500
Wavelength/nm
A$_0$/(A$_0$-A)
22
20
18
16
14
12
10
8
6
4
100
200
300
400
500
600
700
800
1/[Na$^+$]

(b)


TNC + Mg^{2+}
Abs.
1.2
0.9
0.6
0.3
0.0
200
300
400
500
600
Wavelength/nm
A$_0$/(A$_0$-A)
30
25
20
15
10
5
0
200
400
600
800
1000
1200
1/[Mg^{2+}]

(c)



(d)

(e)

Fig. S3 Absorption spectra of **TNC** in CH_3CN solution with 0.1 M nBu_4NPF_6 as a function of concentration of metal cations. (a) [**TNC**]: 1.5×10^{-5} mol/L; Li^+: 0~135 equiv; the inset shows the titration curve against [Li^+] by the plot of the absorbance at 338 nm; (b) [**TNC**]: 3.1×10^{-5} mol/L; Na^+: 0~260 equiv; the inset shows the titration curve against [Na^+] by the plot of the absorbance at 395 nm; (c) [**TNC**]: 3.1×10^{-5} mol/L; Mg^{2+}: 0~210 equiv; the inset shows the titration curve against [Mg^{2+}] by the plot of the absorbance at 395 nm; (d) [**TNC**]: 1.4×10^{-5} mol/L; Ca^{2+}: 0~40 equiv; the inset shows the titration curve against [Ca^{2+}] by the plot of the absorbance at 395 nm; (e) [**TNC**]: 1.4×10^{-5} mol/L; Zn^{2+}: 0~400 equiv; the inset shows the titration curve against [Zn^{2+}] by the plot of the absorbance at 335 nm.

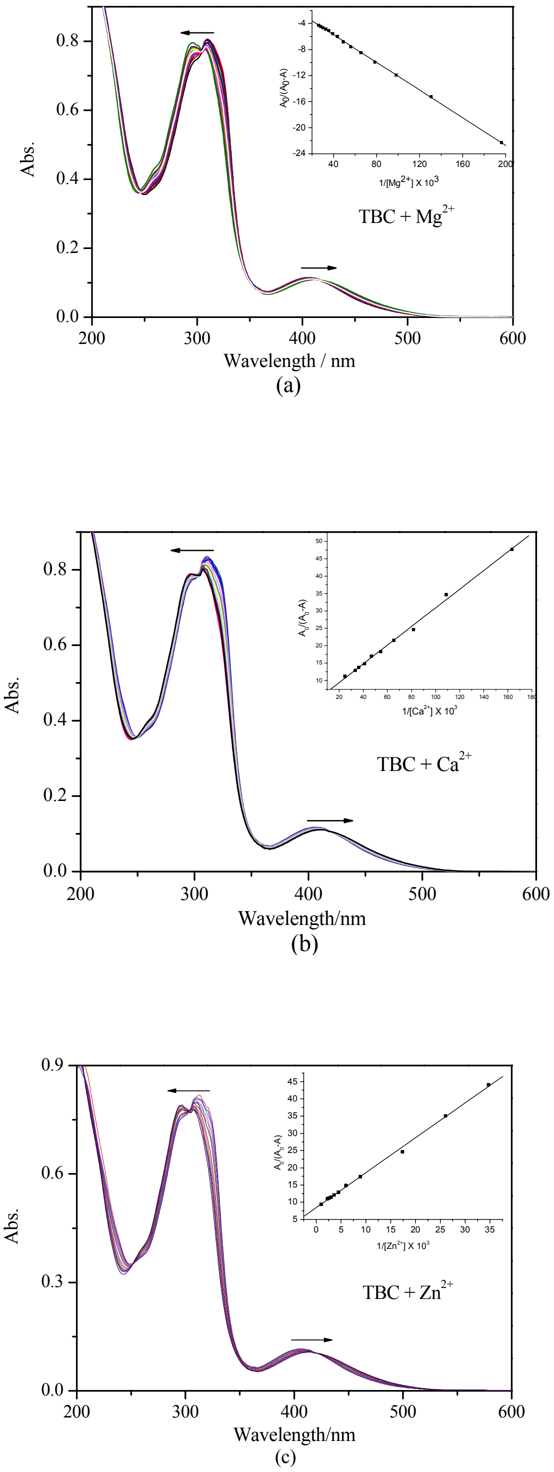
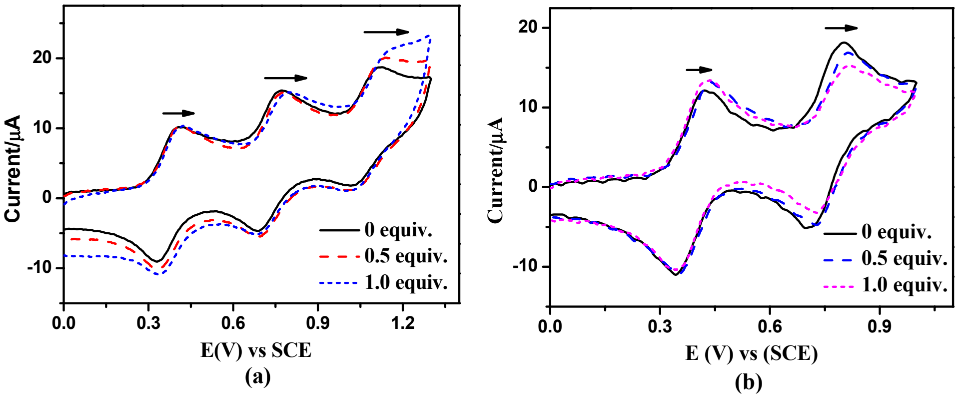


Fig. S4 Absorption spectra of **TBC** in CH_3CN solution with 0.1 M nBu_4NPF_6 as a function of concentration of metal cations. (a) [**TBC**]: 2.4×10^{-5} mol/L; Mg^{2+}: 0~3 equiv; the inset shows the titration curve against $[Mg^{2+}]$ by the plot of the absorbance at 450 nm; (b) [**TBC**]: 2.4×10^{-5} mol/L; Ca^{2+}: 0~1 equiv; the inset shows the titration curve against $[Ca^{2+}]$ by the plot of the absorbance at 405 nm; (c) [**TBC**]: 1.5×10^{-5} mol/L; Zn^{2+}: 0~41 equiv; the inset shows the titration curve against $[Zn^{2+}]$ by the plot of the absorbance at 406 nm.



(a) (b)

Fig.S5 Cyclic voltammogram of **TNC** (a) and **TBC** (b) (10^{-3} M) as a function of Pb^{2+} concentration, recorded in a mixture of CH_3CN with $^{n}Bu_4NPF_6$ (0.1 M) as the supporting electrolyte.

References

1 a) Wang, C. S.; Ellern, A.; Khodorkovsky, V.; Bernstein, J.; Becker, J. Y. *J. Chem. Soc., Chem. Commun.* 1994, 983. b) Green, D. C. *J. Org. Chem.* 1979, **44**, 1476. c) W. S. Tang, X. X. Lu, K. M. C. Wong, V. W. W. Yam, *J. Mater. Chem.*, 2005, **15**, 2714; d) E. M. Hyde, B. L. Shaw, I. Shepherd, *J. Chem. Soc., Dalton Trans.*, 1978, 1696; e) K. Kikukawa, G. X. He, A. Abe, T. Goto, R. Arata, T. Ikeda, F. Wada, T. Matsuda, *J. Chem. Soc., Perkin Trans. 2*, 1987, 135.

2 Connors, K. A. Binding Constant: the Measurement of Molecular Complex Stability; John Wiley & Sons: New York, 1987