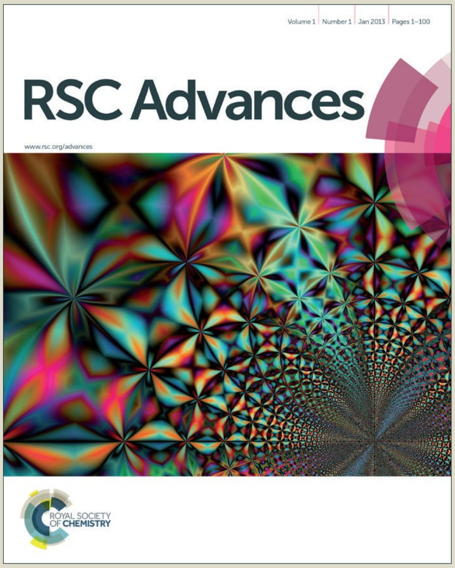
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

COMMUNICATION

Terpyridinyl Dibenzo[b,d]furan and Dibenzo[b,d]thiophene based Tetrameric *Bis*metallo-macrocycles

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

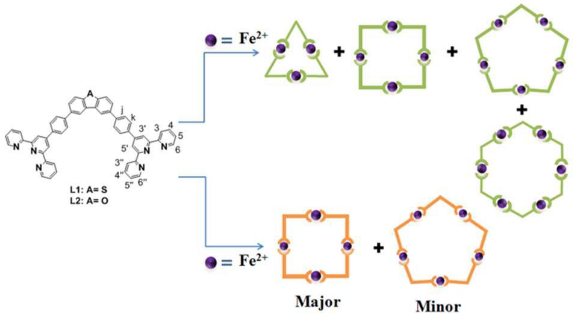
www.rsc.org/

Tun Wu,[a]† Guo Yuan,[a]† Die Liu,[a] Meng Wang,[a] Yiming Li,[a] Mingzhao Chen,[a] Hongwen Tao[b] and Pingshan Wang[a]*

Novel *di*benzo[b,d]thiophene and *di*benzo[b,d]furan-based *bis*terpyridine ligands have been synthesized and used to create unique metallomacrocycles. Directly self-assembly between the *bis*terpyridine ligands and Fe^{2+} led to a mixture containing multiple *homo*-metallomacrocycles. However, utilizing the robust Tpy(TpyRu^{2+}Tpy)Tpy ligands, the metallo-organic ligands, coordination with Fe^{2+} resulted in the pure tetrameric *bis*metallo-macrocycles. Structures were characterized by ^{1}H-NMR, COSY-NMR, DOSY-NMR, ESI-TOF-MS and UV/vis spectrum.

Over the past two decades, the design and construction of highly ordered, supramolecular architectures have attracted considerable attention, especially metallic macrocycles.[1] The innovative works of Lehn,[2-4] Stang,[5-6] Fujita,[7] Newkome[7] and many others[8-11] in the field of self-assembly have shown that understanding the nature of the intermediate is an important tool in determining the outcome of the final supramolecular structure. In terms of a coordination-driven approach to supramolecular structures, there is growing concern with the 2,2’:6’,2’’-terpyridine ligands as a building block due to its strong binding with many transition metal ions,[12-14] metallomacrocycles with trigonal-,[15-17] quadrilateral-,[18-21] pentagonal-,[22-23] and hexagonal-shaped[24-27] motifs have been achieved by utilizing *poly*terpyridine-based metallo-ligand self-assembly methods. However, terpyridine-based organic ligand is more flexible than expected which could lead to the formation of multicomponent mixture.[27]

Herein, we describe our approach to synthesizing a unique set of macrocycles employing two novel *bis*terpyridine ligands (**L1** and **L2**) based on *di*benzo[b,d]thiophene and *di*benzo[b,d]furan units. The angels of **L1** and **L2** are approximately 79.5° and 90°, respectively, and this becomes of apparent significance upon complexation.[28] The ability of **L1** to self-assemble with Fe^{2+} generated mixed macrocycles with metallocycles ranging from triangular to hexameric in nature; however, coordination of **L2**, due to its close 90° bond angle, with Fe^{2+} yielded only a tetrameric cycle and small amounts of a pentameric cycle (Scheme **1**). In order to construct single quantities of metallo-macrocycles, a step-wise approach was employed. First, a half-square bracket metallo-organic ligand (**D3** and **D4**, Scheme **2**) with two uncomplexed free terpyridines was constructed; thereafter, when coordinated with Fe^{2+}, nearly quantitative yields of two dinuclear tetrameric cycles were obtained.



Scheme **1.** Directmetallo-macrocyclic assemblies from ligand **L1** or **L2** and Fe^{2+}.

Synthesis of the key organic building blocks (**L1** and **L2**) began by altering commercially available *di*benzo[b,d]thiophene and *di*benzo[b,d]furan to give 2,8-dibromodibenzo[b,d]thiophene and 2,8-dibromodibenzo[b,d]furan.[29] Subsequent reaction with (4-([2,2':6',2''-terpyridin]-4'-yl)phenyl)boronic acid[21] via Suzuki-coupling yielded the desired ligands (see ESI, Scheme S1). The ligands were structurally confirmed by ^{1}H-NMR (Fig S1-S2), ^{13}C-NMR (Fig S11-S12) and LC-MS (Fig S15, Fig S16).

L1 reacted with 1 equiv. of FeCl$_2$ in a mixed solvent (CHCl$_3$/MeOH=1/1) to produce an inseparable metallo-macrocyclic mixture (Scheme **1** and Fig **1**). The mixed structures were confirmed by ^{1}H-NMR, (Fig **1**, top) showing the most characteristic peak of tpyH$^{3',5'}$ revealed in multiple peaks. In addition, ESI-TOF-MS indicated the multi-macrocycles (**L1**Fe)$_x$ by revealing the metallo-trimer (m/z= 427.266, 541.513, 713.136 and 999.179 corresponding to [(**L1**Fe)$_3$-nPF$_6$]$^{n+}$, n=3-6), metallo-tetramer (m/z= 508.824, 617.79 and 779.344 corresponding to [(**L1**Fe)$_4$-nPF$_6$]$^{n+}$, n=5-7), metallo-pentamer (m/z= 490.663, 570.117, 672.274 and 808.481 corresponding to [(**L1**Fe)$_5$-nPF$_6$]$^{n+}$, n=6-9), and trace amounts of the

---

[a] College of Chemistry and Chemical Engineering, Central South University, Changsha-410083, Hunan, China. Fax: 0086-731-88879616; Tel: 0086-731-88879616; E-mail: chemwps@csu.edu.cn.
[b] College of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan-411201, Hunan, China.

† These author contributed equally to this work.

Electronic Supplementary Information (ESI) available: [details of 1H NMR, 2D COSY, MS, Isotope Parttern and UV data were included here]. See DOI: 10.1039/x0xx00000x

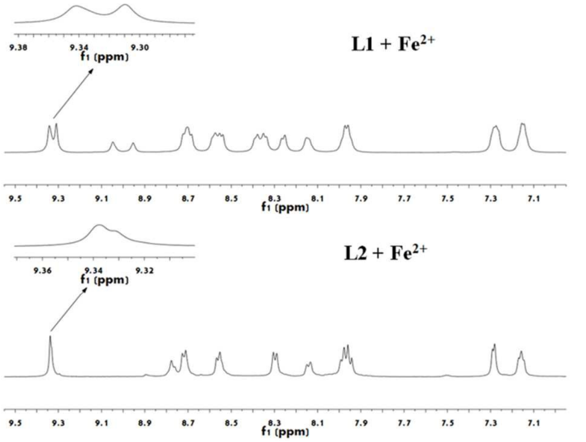


Fig **1**. ^{1}H-NMR of metallo-macrocycles [(**L1**Fe)$_x$ (top) and (**L2**Fe)$_x$ (bottom)] from directly self-assembly with Fe^{2+}.

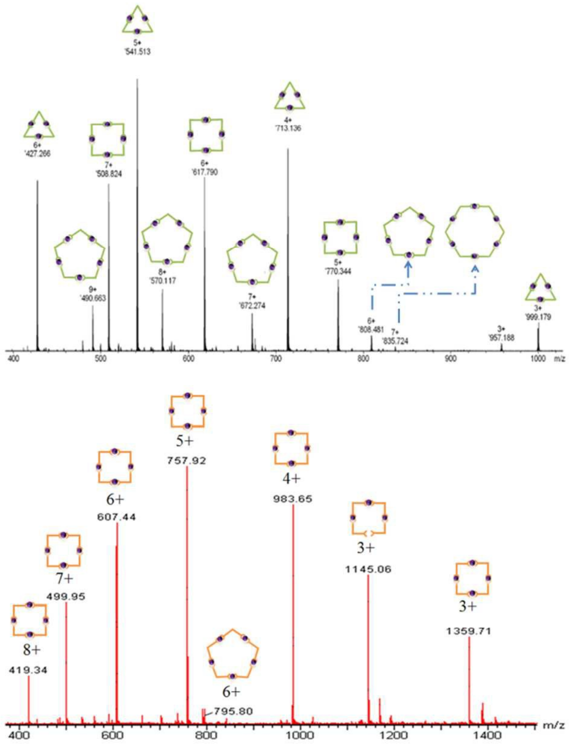
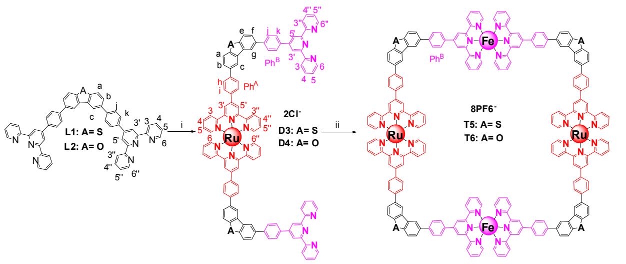


Fig **2**. ESI-TOF-MS spectrum of (**L1**Fe)$_x$ (top) and (**L2**Fe)$_x$ (bottom).

metallo-hexamer (m/z= 835.724 corresponding to [(**L1**Fe)$_6$-7PF$_6$]$^{7+}$)(Fig **2**, top).

When treating **L2** with 1 equiv. of FeCl$_2$, ^{1}H-NMR showed multiple peaks corresponding to the tpy$H^{3',5'}$ proving that the product also is a mixture, but more distinguishable than (**L1**Fe)$_x$ (Fig **1**, bottom). The ESI-TOF-MS spectrum confirmed a main product of the metallo-tetramer (m/z= 419.34, 499.95, 607.44, 757.92, 983.65 and 1359.71 corresponding to [(**L2**Fe)$_4$-nPF6]$^{n+}$, n=3-8) and trace amounts of the metallo-pentamer (m/z=795.80 corresponding to [(**L2**Fe)$_5$-4PF$_6$]$^{6+}$) (Fig **2**, bottom). The most likely reason is the extended phenyl group in **L1** increased the rotation and bending flexibility, leading to the diversity in the molecular coordination.[21] In the results from **L2**, the angel was much closer to 90° which decreased the rotational freedom during the self-assembly process.



Scheme **2**. Synthetic Route of bismetallo-tetramers **T5** and **T6**, red parts represent Ru^{2+} complexed terpyridines (Tpy-A), purple represents terpyridines complexed with Fe^{2+} (Tpy-B). Reagents and conditions: (i) 0.5equiv of RuCl$_3$, reflux, 48 h; (ii) FeCl$_2$, reflux, 12 h.

It has been reported that the [Tpy-Ru-Tpy]$^{2+}$ structure[21] is strong enough to obstruct scrambling of ligands. Thus, a step-wise coordination method was used for the design and synthesis of metallo-dimmers [(**L1**Ru**L1**)Cl$_2$] and [(**L2**Ru**L2**)Cl$_2$] (**D3** and **D4**) from a one-pot reaction. ^{1}H-NMR of dimer **3** (**D3**) exhibited two distinct resonances of tpy$H^{3',5'}$ at 9.29 ppm and 8.75 ppm with an integration ratio of 1:1 as expected. In addition, peaks at *m/z*= 566.5, 849.2 for [M-2Cl$^-$+H$^+$]$^{3+}$, [M-2Cl$^-$]$^{2+}$ (ESI, Fig. S17) also provided evidence for the formation of **D3**. In terms of **D4**, along with consistent ^{1}H-NMR spectra, two distinct resonances of tpy$H^{3',5'}$ were at 9.54 ppm and 8.87 ppm with an integration ratio of 1:1, ESI-TOF-MS showed peaks at *m/z*= 417.1, 555.8 and 833.2 for [M-2Cl$^-$+2H$^+$]$^{4+}$, [M-2Cl$^-$+H$^+$]$^{3+}$ and [M-2Cl$^-$]$^{2+}$ respectively (Fig S18).

Subsequently, **D3** and **D4** were treated with FeCl$_2$ in MeOH. After the simple counterion exchange with NH$_4$PF$_6$, two desired metallo-tetramers were obtained in nearly quantitative yield (Scheme 2). The ^{1}H-NMR spectra for metallo-tetramer **5** (**T5**, Fig 2), where the color denotes the respective metals, displayed two resonances of tpy$H^{3',5'}$ for each assignable proton, all integrating 1:1. In comparison to **D3**, protons at the 6,6'' position of Tpy-B (purple) exhibited a dramatic shift from 8.71to 7.29 ppm due to the electron shielding effect after complexation with Fe^{2+} (Fig. 3, Fig. S5 and S9). ^{1}H-NMR for metallocycle **6** (**T6**) presented a similar situation in which protons at the 6,6'' position of Tpy-B (purple) shifted upfield from 8.79 ppm to 7.29 ppm (Fig 4, Fig S6 and S10). The whole aromatic region displayed two resonances for each assignable proton with an integration ratio of 1:1. All of the assignable were based on 2D COSY NMR.

2D DOSY-NMR spectroscopy has frequently been utilized to determine the purity of the complexes due to its effective

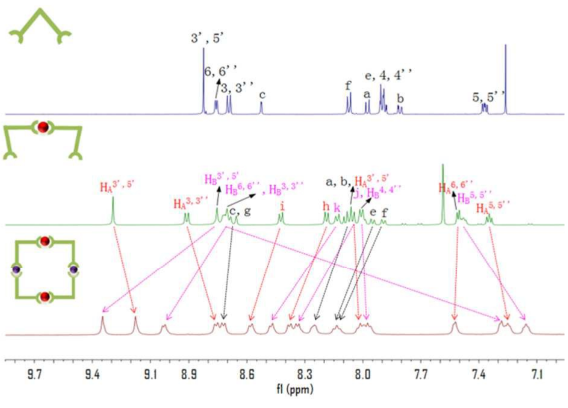


Fig **3**. Stacked ^{1}H-NMR spectra of **L1** (CDCl$_3$), **D3** (CDCl$_3$: CD$_3$OD=1:1), **T5** (CD$_3$CN), where Ru^{2+} represented as the red balls, Fe^{2+} as the purple balls.

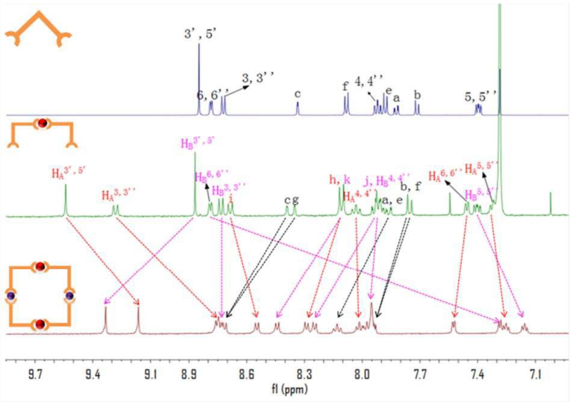


Fig **4**. Stacked ^{1}H-NMR spectra of **L2** ($CDCl_3$), **D4** ($CDCl_3$: CD_3OD=1:1), **T6** (CD_3CN), where Ru^{2+} represented as the red balls, Fe^{2+} as the purple balls.

characterization for molecules having relatively larger molecular weights and for monitoring self-assembly processes by correlating chemical resonances to diffusion coefficients in solutions.[30] **T5** and **T6** (Fig **5**) showed only one component in solution for each substance. The diffusion coefficients measured in CD_3CN at 298K are 2.796 × 10^{-10} m^2/s for T5, and 2.759 × 10^{-10} m^2/s for T6, respectively. Experimental hydrodynamic radius for **T5** and **T6** were calculated to be 2.13 nm and 2.16 nm via the Stoke-Einstein equation $D = kBT/6\pi\eta r_H$ (kB, Boltzman constant; T, absolute temperature; η = 0.367 mPa·s, viscosity of CD_3CN at 298 K).[31]

Further support for the formation of **T5** was provided by ESI-TOF-MS signals for the multiply-charged species in charge states +8 (m/z 438.21), +7 (m/z 521.9673), +6 (m/z 633.2730), +5 (m/z 788.92), +4 (m/z 1022.39) and +3 (m/z 1401.22). The detected results and the isotope pattern of each peak agreed well with the corresponding theoretical distributions (Fig **6** top, also see ESI). In terms of **T6**, there are several unambiguous peaks for the multiply-charge states +8 (m/z 430.72), +7 (m/z 512.97), +6 (m/z 622.62), +5 (m/z 776.14) +4 (m/z 1006.41), +3 (m/z 1390.21). Likewise, slight differences between the detected isotope pattern and the corresponding theoretical distributions of each peak have been found (Fig **6** bottom, also see ESI).

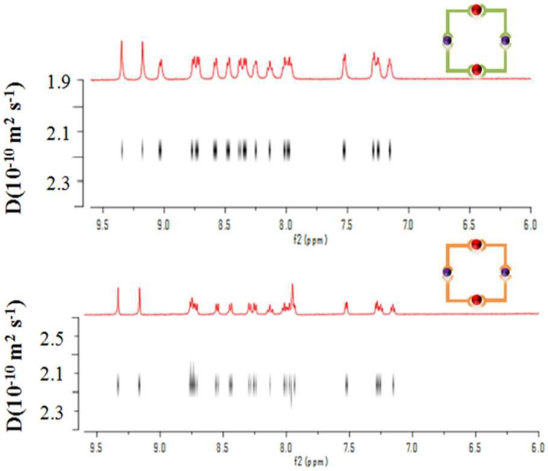


Fig **5**. 2D DOSY-NMR spectra of **T5** (up) and **T6** (bottom).

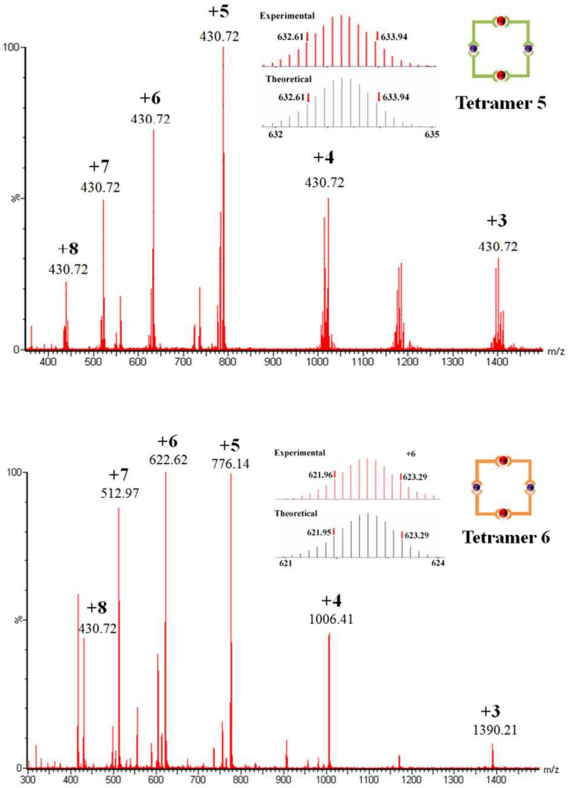


Fig **6**. ESI-TOF-MS spectra of **T5** (up) and **T6** (bottom).

UV-vis spectroscopy for the compounds were examined in MeCN. For **D3**, the major absorption band at λ= 310 nm originated from intra-ligand charge transfer in addition to the characteristic absorption band at λ= 496 nm indicating the MLCT of Ru^{2+} to terpyridine ligands. Further, **T5** revealed two MLCT bands, λ= 494 and 572 nm, representing Ru^{2+} and Fe^{2+}, respectively (Fig **7** left, Fig S22). As well, the similar UV-vis spectra of **D4** and **T6** were illustrated in Fig 7 (right, Fig S23). The electrochemical properties of complexes **T5** and **T6** were investigated by cyclic voltammetry (see ESI, Fig. S24), all complexes illustrated one reversible oxidation couple of Ru^{2+}/Ru^{3+} and the moderate onset oxidation potentials, which was determined to be 1.50 V (**T5**) and 1.70 V (**T6**) *vs* Hg/Hg_2Cl_2, respectively. In addition, the reversible oxidation couple of Fe^{2+}/Fe^{3+} were measured to be 0.73V in **T5** and 1.15V in **T6**, respectively.

Conclusions

In conclusion, two dibenzo[b,d]thiophene and dibenzo[b,d]furan-based bisterpyridinyl ligands possessing uniquely

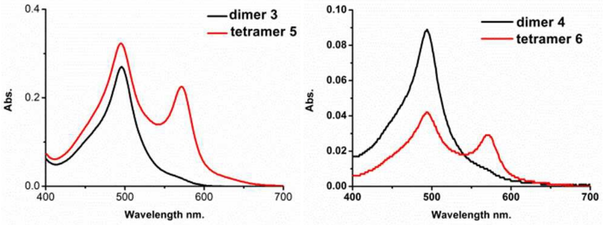


Fig **7**. Partial UV spectrum of **D3**, **T5** (left) and **D4**, **T6** (right).

restricted angles, have been synthesized and proven to self-assemble with transition metals to form two dinuclear tetrameric metallomacrocycles by means of a step-wise strategy. The structures of the two metallo-tetramers were confirmed by ^{1}H-NMR, COSY-NMR, DOSY-NMR, ESI-TOF-MS and UV-vis. This study demonstrates that controlling the angled metallo-ligands is possible for the purpose of preparing pure square-shaped supramolecular metallomacrocycles. It provides an effective method to further probe the characteristics, structure and stability of $[\mathrm{TpyRuTpy}]^{2+}$ compounds in order to design and prepare Ru-based terpyridine complexes with enhanced photophysical properties.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (21274165) and the Distinguished Professor Research Fund from Central South University of China. The authors gratefully acknowledge Dr. Carol D. Shreiner for her professional consultation. Authors acknowledge the NMR measurements from The Modern Analysis and Testing Center of CSU.

Notes and references

1 J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim 1995; U. S. Schubert, H. Hofmeier and G. R. Newkome, *Modern Terpyridine Chemistry*, Wiley-VCH, Weinheim, 2006; L. Cronin, *Annu. Rep. Prog. Chem., Sect. A.*, 2004, **100**, 323-383.

2 M. Ruben, U. Ziener, J. M. Lehn, V. Ksenofontov, P. Gutlich and G. B. M. Vaughan, *Chem. Eur. J.*, 2005, **11**, 84-100.

3 M. Barboiu, G. Vaughan, R. Graff and J. M. Lehn, *J. Am. Chem. Soc.*, 2003, **125**, 10257-10265.

4 M. Ruben, J. Rojo, F. J. Romero-Salguero, L. H. Uppadine and J. M. Lehn, *Angew. Chem., Int. Ed.*, 2004, **43**, 3644-3662.

5 S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853.

6 R. Chakrabarty, P. S. Mukherjee and P. J. Stang, *Chem. Rev.*, 2011, **111**, 6810–6918.

7 M. Fujita and K. Ogura, *Coord. Chem. Rev.*, 1996, **148**, 249.

8 L. R. MacGillivray and J. L. Atwood, *Angew. Chem. Int. Ed.*, 1999, **38**, 1018.

9 B. J. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022; E. Baranoff, J. P. Collin, L. Flamigni and J. P. Sauvage, *Chem. Soc. Rev.,* 2004, **33**, 147; E. C. Constable, C. E. Housecroft, M. Neuburger, S. Schaffner and C. B. Smith, *Dalton Trans.*, 2005, **13**, 2259; J. M. Lehn, *Chem. Soc. Rev.*, 2007, **36**, 151; N. Giuseppone, J. L. Schmitt, L. Allouche and J. M. Lehn, *Angew. Chem., Int. Ed.,* Engl., 2008, **47**, 2235; R. S. Forgan, J. P. Sauvage and J. F. Stoddart, *Chem. Rev.*, 2011, **111**, 5434; I. A. Riddell, Y. R. Hristova, J. K. Clegg, C. S. Wood, B. Breiner and J. R. Nitschke, *J. Am. Chem. Soc.*, 2013, **135**, 2723; A. M. Castilla, W. J. Ramsay and J. R. Nitschke, *Acc. Chem. Res.*, 2014, **47**, 2063; P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502; M. Yoshizawa, K. Kumazawa and M. Fujita, *J. Am. Chem. Soc.*, 2005, **127**, 13456; P. Mobian, J.-M. Kern and J.-P. Sauvage, *J. Am. Chem. Soc.*, 2003, **125**, 2016; F. Ibukuro, T. Kusukawa and M. Fujita, *J. Am. Chem. Soc.*, 1998, **120**, 8561; A. E. V. Gorden, J. Xu, K. N. Raymond and P. Durbin, *Chem. Rev.*, 2003, **103**, 4207; T. R. Cook, V. Vajpayee, M. H. Lee, P. J. Stang and Chi, K.-W. *Acc. Chem. Res.*, 2013, **46**, 2464; S. J. Cantrill, K. S. Chichak, A. J. Peters and J. F. Stoddart, *Acc. Chem. Res.*, 2005, **38**, 1; M. Barboiu, G. Vaughan, R. Graff and J.-M. Lehn, *J. Am. Chem. Soc.*, 2003, **125**, 10257; M. Fujita, N. Fujita, K. Ogura and K. Yamaguchi, *Nature*, 1999, **400**, 52; M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417; P. J. Stang, *Chem.–Eur. J.*, 1998, **4**, 19; R. Ziessel, *Synthesis*, 1999, **11**, 1839; M. Wang, C. Wang, X. Q. Hao, J. Liu, X. Li, C. Xu, A. Lopez, L. Sun, M. P. Song, H. B. Yang and X. Li, *J. Am. Chem. Soc.*, 2014, **136**, 6664.

10 S. J. Lee, A. Hu and W. Lin, *J. Am. Chem. Soc.*, 2002, **124**, 12948.

11 H. Jiang and W. Lin, *J. Am. Chem. Soc.*, 2003, **125**, 8084.

12 D. Armspach, M. Cattalini, E. C. Constable, C. E. Housecroft, D. Phillips, *Chem. Commun.*, 1996, 1823.

13 G. R. Newkome, E. He, L. A. Godinez and G. R. Baker, *J. Am. Chem. Soc.*, 2000, **122**, 9993.

14 A. Wild, A. Winter, F. Schlutter, U.S. Schubert, *Chem. Soc. Rev.*, 2011, **40**, 1459.

15 S. H. Hwang, C. N. Moorefield, F. R. Fronczek, O. Lukoyanova, L. Echegoyen and G. R. Newkome, *Chem. Commun.*, 2005, **6**, 713-715.

16 K. Mahata, M. L. Saha and M. Schmittel, *J. Am. Chem. Soc.*, 2010, **132**, 15933-15935.

17 M. Schmittel and K. Mahata, *Chem. Commun.*, 2010, **46**, 4163-4165.

18 K. Mahata and M. Schmittel, *J. Am. Chem. Soc.*, 2009, **131**, 16544-16554.

19 R. D. Sommer, A. L. Rheingold, A. J. Goshe and B. Bosnich, *J. Am. Chem. Soc.*, 2001, **123**, 3940-3952.

20 E. C. Constable, B. A. Hermann, C. E. Housecroft, M. Neuburger, S. Schaffner and L. J. Scherer, *New J. Chem.*, 2005, **29**, 1475-1481.

21 J. L. Wang, X. Li, X. Lu, I. F. Hsieh, Y. Cao, C. N. Moorefield, C. Wesdemiotis, S. Z. D. Cheng and G. R. Newkome, *J. Am. Chem. Soc.*, 2011, **133**, 11450-11453; Y. Li, Z. Jiang, J. Yuan, D. Liu, T. Wu, C. N. Moorefield, G. R. Newkome and P. Wang, *Chem. Commun.* 2015, **51**, 5766.

22 S. H. Hwang, P. S. Wang, C. N. Moorefield, L. A. Godinez, J. Manriquez, E. Bustos and G. R. Newkome, *Chem. Commun.*, 2005, **37**, 4672-4674.

23 Y. T. Chan, C. N. Moorefield, M. Soler and G. R. Newkome, *Chem. Eur. J.* 2010, **16**, 1768-1771.

24 Y. T. Chan, X. Li, M. Soler, J. L. Wang, C. Wesdemiotis and G. R. Newkome, *J. Am. Chem. Soc.*, 2009, **131**, 16395-16397.

25 G. R. Newkome, T. J. Cho, C. N. Moorefield, G. R. Baker, R. Cush and P. S. Russo, *Angew. Chem., Int. Ed.*, 1999, **38**, 3717-3721.

26 V. Stepanenko and F. Wurthner, *Small*, 2008, **4**, 2158-2161.

27 S. Perera, X. Li, M. Guo, C. Wesdemiotis, C. N. Moorefield and G. R. Newkome, *Chem. Commun.*, 2011, **47**, 4658-4660. Y. T. Chan, X. Li, C. Wesdemiotis, C. N. Moorefield and G. R. Newkome, *Chem. Eur. J.* 2011, **17**, 7750 – 7754.

28 K. Suzuki, M. Tominaga, M. Kawano and M. Fujita, *Chem. Commun.*, 2009, **13**, 1638-1640.

29 S. L. Zhang, R. F. Chen, J. Y, F. Liu, H. J. Jiang, N. E. Shi, Z. F. An, C. Ma, B. Liu and W. Huang, *Org. Lett.*, 2010, **12**, 3438–3441.

30 Y. Cohen, L. Avram and L. Frish, *Angew. Chem., Int. Ed.*, 2005, **44**, 520–554.

31 H. Lee, R. M. Venable, A. D. Jr. MacKerrell and R. W. Pastor, *Biophys. J.*, 2008, **95**, 1590–1599.

Terpyridinyl Dibenzo[b,d]furan and Dibenzo[b,d]thiophene based Tetrameric *Bis*metallo-macrocycles

Tun Wu, Yuan Guo, Die Liu, Meng Wang, Yiming Li, Mingzhao Chen, Hongwen Tao and
Pingshan Wang

Publication Date (Web): 2015 (Communication)
DOI:xxx

RSC Advances, **2015**.

Dibenzo[b,d]thiophene and dibenzo[b,d]furan based *bis*terpyridines having specific bend angles had been synthesized. Directly self-assembly between the *bis*terpyridines and Fe^{2+} led to the metallo-macrocyclic mixtures. Utilizing the robust metallo-organic-ligands result the pure tetrameric metallo-macrocycles.