Thiophene-Coated Functionalized M₁₂L₂₄ Spheres: Synthesis, Characterization, and Electrochemical Properties

Fei Jiang, Ning Wang, Zhengkun Du, Jun Wang, Zhenggang Lan, and Renqiang Yang*^[a]

Precise self-assembly reactions to synthesize supramolecular complexes and coordination polymers with novel structures and functional properties have attracted considerable interests by chemists.^[1,2] One big challenge of self-assembly is to create well-defined nanoscale complexes with controllable sizes and shapes. In recent years, the coordinationdriven self-assembly method was proposed as a powerful alternative technique to perform the efficient synthesis of multifunctional molecules. For example, Stang and co-workers reported a facile synthetic route to prepare snowflakeshaped metallodendrimers with hexagonal cavities as their cores.^[1d] Fujita and co-workers succeeded in the self-assembly of the first artificial sphere-in-sphere molecule.^[2j] Thiophene-based molecules and polymers are great promising functional materials for photovoltaic cells,^[3,4] pharmaceuticals,^[5] and dyes.^[6] However, traditional synthetic routes often give low product yields and largely disordered structures of the thiophene derivatives. Meanwhile, functional thiophene derivatives, especially those applied to supramolecular self-assembly, have hardly been reported. Stimulated by these ideas, we envision that when the thiophene functional group is attached at the vertex of a bidentate ligand that is combined with an appropriately designed palladium(II)-containing compound, it will provide access to a new family of multifunctional spherical structures. Moreover, this strategy allows us to control precisely the shape and size of resulting spheres, the total number of incorporated functional moieties (thiophene), as well as the distribution of the above quantities.^[7] The thiophene units hanging outside of the spheres are the novel functional groups which will make the self-assembled coordination systems exhibit some unique electrochemical properties.

Herein, we report an instant synthesis method to prepare coordination spheres with an exterior surface featuring 24 thiophene functional groups. The shell of each coordination sphere displayed a rigid and well-defined framework that was assembled from twelve 90° metal-containing compounds (M) and twenty-four 120° organic bidentate ligands (L,



Scheme 1. Self-assembly reaction in the preparation of spherical $M_{12}L_{24}$ complex 2 with 24-fold exterior surface appended with 2- or 3-substituted thiophene functional groups.

Scheme 1). Two different thiophene functional groups (2substituted or 3-substituted thiophene) were attached to the 120° bidentate ligands, denoted as **1a** and **1b**, respectively. Thus by linking a thiophene functional group at the vertex of each bent bridging ligand, all 24 thiophene groups were precisely appended outside of the spherical complexes. From starting material 3,5-dibromophenol, bidentate ligands 1a and 1b were obtained with a relatively high yield through four-step reactions (see the Supporting Information, Scheme S1-S2). When ligand 1a (0.1 mmol in acetone) was added into $Pd(NO_3)_2$ acetone solution (0.05 mmol, 0.5 equiv) at room temperature, the thiophene-appended spherical complex 2a precipitated immediately. The reaction process required simple mixing of metals (M) with ligands (L) according to the 12:24 stoichiometric ratio. The self-assembly reaction occurred so quickly that it was completed within just a few seconds, and a rather high yield of 88% was achieved. Such high reaction rates and yields can be explained by the different solubilities of reactants and products. Both the metal precursor $(Pd(NO_3)_2)$ and organic bidentate ligands (1a and 1b) were well soluble in acetone, whereas the resulting coordination spheres (2a and 2b) were insoluble in acetone. Thus the reaction equilibrium moved quickly towards the positive direction, and a high yield of products was achieved within a very short time. Our results indicated that the unique solvent system was very efficient to prepare the self-assembled complexes compared to previously reported ones,^[8] facilitating isolation and purification.

The formation of a single product 2a was qualitatively characterized by ¹H NMR spectroscopic analysis (Figure 1b). Compared to ligand 1a, the ¹H NMR spectrum of

Chem. Asian J. 2012, 00, 0-0

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[[]a] F. Jiang, N. Wang, Z. Du, J. Wang, Prof. Dr. Z. Lan, Prof. Dr. R. Yang Qingdao Institute of Bioenergy and Bioprocess Technology Chinese Academy of Sciences
189 Songling Rd., Qingdao 266101 (China) Fax: (+86)532-8066-2778 E-mail: yangrq@qibebt.ac.cn

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201200413.

COMMUNICATION



Figure 1. ¹H NMR spectrum (600 MHz, $[D_6]DMSO$, 298 K) of a) ligand **1a** and b) sphere **2a**; signals a, b, e, f, and g denote PyHa, PyHb, and 2-substituted thiophene ring protons, respectively, while peaks c and d originate from the benzene ring. c) ¹H DOSY spectrum of **2a** (600 MHz, $[D_6]DMSO$, 298 K).

2a showed only one set of signals, in good agreement with its highly symmetric spherical structure. The peak at 9.5 ppm was assigned to PyHa (peak a, Py=pyridinyl) and the peak at 8.4 ppm was assigned to the superimposed PyHb (peak b) and benzene proton (peak d), and peak c was assigned to the other two protons in the benzene ring. The proton signals e, f, and g corresponded to the three types of protons in the 2-substituted thiophene ring. The large down-

field shifts of signals on the asite and b-site protons in the pyridine group (e.g., $\Delta \delta =$ 0.81 ppm and 0.54 ppm, respectively) can be ascribed to strong Pd-N coordination interactions.^[9] The broadening of the signals in the ¹H NMR and DEPT Q NMR spectra (Figure 1b and Figures S5, S6 in the Supporting Information) reflects the slow dynamic motion of the rigid large cores.^[10] Similar results were obtained for 2b. Elemental analysis of 2a and 2b provided further evidence to support the formation of current spherical structures (see the Supporting Information for details).

Diffusion-ordered NMR spectroscopy (DOSY) further confirmed the selective formation of a single species. The proton signals of **2a** showed a single diffusion coefficient at $1.66 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ (log D = -9.78; Figure 1 c). According to the Stokes-Einstein equation,^[11] the diameter of sphere **2a** was estimated to be 4.3 nm. Similarly, sphere **2b** was assembled from 3-substituted thiophene ligand **1b** and Pd(NO₃)₂. The diffusion coefficient in [D₆]DMSO determined by DOSY experiment was $1.58 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$ (log D = -9.80), almost the same value as for sphere **2a** (see Figure S12 in the Supporting Information). This result indicated that the two spheres (**2a** and **2b**) were nearly equal size, despite the different substitution positions in the thiophene ring.

The spherical structure of 2a was also ascertained directly by AFM (Figure 2), which clearly showed that the spherical complex 2a comprised 4-5 nm molecular particles. For both 2a and 2b, the sizes of the supramolecular nanospheres were in agreement with those obtained from DOSY deduced results and theoretical calculations at the semi-empirical PM₆ level using Gaussian 09 package^[12] (Figure 3 and Figures S16 and S17 in the Supporting Information). The structure of 2a and 2b was clearly a highly symmetric cuboctahedron structure, which may be viewed as a cube that has every vertex truncated to generate eight triangular faces. The theoretical calculations showed that the diameter and the longest Pd-Pd distance of sphere 2a were 4.8 nm and 2.7 nm, respectively. Both of the spherical complexes (2a and 2b) had 24 thiophene units equivalently appended on the periphery of the spheres.

Similar synthetic ideas were employed to synthesize endohedral thiophene-based functional ligands 1c and 1d (Scheme 2) according to the same procedure as for 1a and 1b (see the Supporting Information and Scheme S4 for details). However, endohedral functional spheres were not ob-



Figure 2. AFM images of 2a on mica, a) 3D image, b) 2D image, and c) height profile.

www.chemasianj.org

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

FF These are not the final page numbers!



Figure 3. Simulated molecular model of spheres 2a and 2b optimized at the semi-empirical PM6 level using Gaussian 09 package.



Scheme 2. Molecular structures of ligands 1c and 1d.

tained. This result was probably due to steric repulsion between the pyridyl groups and the benzene rings.^[13] For example, ligand 1c perhaps adopted unfavorable nonplanar conformation and did not assemble into the M12L24 complex upon complexation with Pd^{II} compounds. Thus the four pyridyl groups should display a perpendicular array with respect to the PdN₄ plane, which seems to be essential to the self-assembly of the spherical complex.

The electrochemical properties of 24-fold spherical complexes (2a and 2b) were investigated. To explore the role of coordination effects, the voltammetric behaviors of sphere 2b and ligand 1b in DMSO were measured at concentrations of 0.3 mm and 7.2 mm (24 equiv), respectively. Their cyclic voltammograms were obtained in the potential range from -2.0 to +2.0 V at a scan rate of 100 mV s^{-1} . As shown in Figure 4a, the reduction potential (E_{pc}) of ligand **1b** was -1.212 V, and the reduction potential (E_{pc}) of sphere **2b** was -1.059 V. In other words, the potential peak was positively shifted by 0.153 V from 1b to 2b. We assumed that the positive shift was perhaps due to the cationic status of spheres after coordination. However, the nearly identical peak currents (i_{pc}) of ligand **1b** and sphere **2b** simply reflected the similar numbers of 2-substituted thiophene moieties in 1b and 2b, since the concentration of 2-substituted thiophene functional groups in 1b (7.2 mm) was equivalent to that of sphere 2b (0.3 mm). Sphere 2b showed only one broad reduction potential, indicating that no interaction existed among the multiple redox centers at the periphery of the sphere.^[14] The reduction currents (i_{pc}) of sphere **2b** increased linearly with the square root of the sweep rate from 50 to



Figure 4. a) The cyclic voltammograms of ligand 1b and sphere 2b at a scan rate of 100 mVs⁻¹, b) the cyclic voltammograms of sphere 2b at scan rates of 50, 75, 100, 125, 150, 175 and 200 mV s⁻¹, respectively. Solution: 7.2 mm 1b and 0.3 mm 2b in DMSO. Results are reported versus Ag/AgCl. Inset: linear curve of the reduction current (i_{pc}) versus the square root of the sweep rate $(v^{1/2})$.

200 mVs⁻¹ (Figure 4b and inset). This finding indicated that a diffusion-controlled redox process took place for sphere 2b. Similar results were obtained for sphere 2a (see Figure S13 in the Supporting Information). It is worth noting that both **1a** and **2a** had larger reduction currents (i_{pc}) than 1b and 2b, respectively, at the same concentration. For example, the peak current (i_{pc}) of sphere **2a** was $4.562 \times$ 10^{-5} A, while the i_{pc} of sphere **2b** was 2.418×10^{-5} A at the same concentration (0.3 mm). We deduced that the 2-substituted thiophene functional complexes can diffuse more easily to the electrode than those with 3-substituted thiophene functional groups. Cyclic voltammograms of sphere 2a also showed a broad voltammetric peak, which probably resulted from the multielectron transfer process that occurred simultaneously. No decomposition of the complexes during these redox processes was observed, as indicated by the examination of the ¹H NMR spectra of **2a** and **2b** before and after the redox studies.

In summary, an instant self-assembly method was developed to synthesize well-defined spherical complexes, which were assembled from twelve 90° metal subunits (M) and twenty-four 120° organic bidentate ligand subunits (L) in acetone. The unique solvent system was confirmed as an efficient, simple method to prepare the self-assembled complexes compared to previously reported ones, facilitating isolation and purification. The spherical complexes have been characterized by NMR spectroscopy, elemental analy-

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemasianj.org

I.

3

These are not the final page numbers! **77**

COMMUNICATION

sis, AFM images, and theoretical calculations. DOSY NMR spectroscopy, AFM images, and theoretical calculations confirmed the formation of nanoparticles with size 4-5 nm. The hollow core environment provides an ideal cavity for guest encapsulation. Meanwhile, the thiophene functional groups were attached to the vertexes of each ligand, and the obtained spherical complexes exhibited interesting redox properties. Moreover, the bulk properties of this type of novel functional material can be tailored via the development of spherical complexes decorated by other functional groups, such as ferrocene, fluorene, and phthalocyanine moieties. We expect that the combination of functional and encapsulated moieties at the periphery and the interior of the spheres, respectively, will allow such spherical molecules to not only act as host "container compounds" but also possess some electrochemical or photochemical applications, such as multielectron redox catalysts, electrode modifiers, and sensors.

Experimental Section

Materials

Reagents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Sigma–Aldrich Co. All the chemicals were of reagent grade and used without any further purification. The preparation of **1a**, **1b**, **1c**, and **1d** is described in Schemes S2 and S4 in the Supporting Information.

Synthesis of Spherical Complexes 2 a and 2 b

A very fast and simple method was used to prepare the self-assembled complexes **2a** and **2b** compared to reported ones.^[1c] When **1a** or **1b** (0.1 mmol, in 5 mL acetone) was added into $Pd(NO_3)_2$ (0.05 mmol) in acetone (5 mL) at room temperature, the precipitate was obtained immediately. The product was collected by filtration, washed with acetone, and dried in vacuo to give **2a** and **2b** (>80% yield of isolated product).

Structure Characterization

Different NMR (¹H NMR, DEPT Q NMR, and other 2D NMR) spectra were recorded on a Bruker DRX-600 (600 MHz) spectrometer. Tetramethylsilane (CDCl₃ solution) in a capillary served as external standard ($\delta =$ 0 ppm). The DOSY NMR spectra were acquired with the standard pulse program from Bruker Topspin software, ledbpgp2s, using a stimulated echo and the longitudinal eddy current delay, with bipolar sine-shaped gradient pulses and two spoiling gradients. All DOSY NMR spectra were recorded with 32 K time domain data points in t₂ dimension and 16 t₁ increments, 16 transients for each t₁ increment, and a relaxation delay of 1 s. AFM images were obtained on an Agilent 5400 scanning probe microscope using AC mode. Melting points were determined on a WRS-1B Digital Melting Point Apparatus. Elemental analysis was carried out on vario EL cube equipment. Molecular structures were optimized with PM₆ using Gaussian 09 package.

Electrochemical Measurements

Electrochemical measurements were made using a CHI 660D System. The working electrode was a diameter of 3 mm glassy carbon electrode, and there was a platinum wire as counter electrode and an Ag/AgCl (3.0 M KCl) electrode as reference electrode. All electrochemical experiments were carried out in DMSO solutions of $n\text{Bu}_4\text{NPF}_6$ (0.1 M) as supporting electrolyte, which were freed of oxygen by bubbling through high-purity argon before experiments. The concentration of redox molecules in solution was, (1) **1a**, **1b**: 7.2 mM, (2) **2a**, **2b**: 0.3 mM, respectively, and scan rates were indicated in the Figure 4.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21103213, 51173199), the Ministry of Science and Technology of China (2010DFA52310), CAS ("One Hundred Talented Program", and KGCX2-YW-399+9-2), the Department of Science and Technology of Shandong Province (2010GGC10345), and the Qingdao Municipal Science and Technology Program (11-2-4-22-hz). J.W. and Z.L. acknowledge the computing resources in the super-computational center in QIBEBT and SCCAS.

Keywords: electrochemistry • nanostructures • palladium • self-assembly • thiophene

- a) B. Olenyuk, J. A. Whiteford, A. Fechtenkotter, P. J. Stang, Nature 1999, 398, 796–799; b) G. Ungar, Y. S. Liu, X. B. Zeng, V. Percec, W. D. Cho, Science 2003, 299, 1208–1211; c) T. Murase, S. Sato, M. Fujita, Angew. Chem. 2007, 119, 5225–5228; Angew. Chem. Int. Ed. 2007, 46, 5133–5136; d) H. B. Yang, A. M. Hawkridge, S. P. D. Huang, N. Das, S. D. Bunge, D. C. Muddiman, P. J. Stang, J. Am. Chem. Soc. 2007, 129, 2120–2129; e) Y. L. Chen, F. Zhang, B. Zhu, Y. Han, Z. S. Bo, Chem. Asian J. 2011, 6, 226–233; f) H. B. Yang, B. H. Northrop, Y. R. Zheng, K. Ghosh, P. J. Stang, J. Org. Chem. 2009, 74, 7067–7074; g) M. Yoshizawa, J. K. Klosterman, M. Fujita, Angew. Chem. 2009, 121, 3470–3490; Angew. Chem. Int. Ed. 2009, 48, 3418–3438; h) H. Ozawa, M. Kawao, T. Nagata, S. Uno, K. Nakazato, Chem. Asian J. 2010, 5, 2393–2399; j) L. L. Zhu, M. Q. Lu, Q. W. Zhang, D. H. Qu, H. Tian, Macromolecules 2011, 44, 4092–4097.
- [2] a) G. F. Swiegers, T. J. Malefetse, Chem. Rev. 2000, 100, 3483-3537; b) V. Percec, A. E. Dulcey, V. S. K. Balagurusamy, Y. Miura, J. Smidrkal, M. Peterca, S. Nummelin, U. Edlund, S. D. Hudson, P. A. Heiney, D. A. Hu, S. N. Magonov, S. A. Vinogradov, Nature 2004, 430, 764-768; c) W. Han, M. Byun, L. Zhao, J. Rzayev, Z. Q. Lin, J. Mater. Chem. 2011, 21, 14248-14253; d) B. H. Northrop, Y. R. Zheng, K. W. Chi, P. J. Stang, Acc. Chem. Res. 2009, 42, 1554-1563; e) B. L. Chen, S. C. Xiang, G. D. Qian, Acc. Chem. Res. 2010, 43, 1115-1124; f) H. Ahmad, A. Meijer, J. A. Thomas, Chem. Asian J. 2011, 6, 2339-2351; g) H. Li, W. M. Lu, F. Chen, X. Dong, Y. H. Dai, J. Coord. Chem. 2010, 63, 106-114; h) K. Suzuki, S. Sato, M. Fujita, Nat. Chem. 2010, 2, 25-29; i) L. Welte, A. Calzolari, R. Di Felice, F. Zamora, J. Gomez-Herrero, Nat. Nanotechnol. 2010, 5, 110-115; j) Q. F. Sun, T. Murase, S. Sato, M. Fujita, Angew. Chem. 2011, 123, 10502-10505; Angew. Chem. Int. Ed. 2011, 50, 10318-10321; k) P. Chithra, R. Varghese, K. P. Divya, A. Ajayaghosh, Chem. Asian J. 2008, 3, 1365-1373; 1) L. J. Chen, Q. J. Li, J. M. He, H. W. Tan, Z. Abliz, H. B. Yang, J. Org. Chem. 2012, 77, 1148-1153.
- [3] a) Y. F. Li, Y. P. Zou, Adv. Mater. 2008, 20, 2952–2958; b) O. L. Muskens, J. G. Rivas, R. E. Algra, E. Bakkers, A. Lagendijk, Nano Lett. 2008, 8, 2638–2642; c) Z. J. Ning, H. Tian, Chem. Commun. 2009, 5483–5495.
- [4] a) R. Q. Yang, A. Garcia, D. Korystov, A. Mikhailovsky, G. C. Bazan, T. Q. Nguyen, J. Am. Chem. Soc. 2006, 128, 16532–16539;
 b) J. Y. Lee, W. S. Shin, J. R. Haw, D. K. Moon, J. Mater. Chem. 2009, 19, 4938–4945;
 c) R. Q. Yang, H. B. Wu, Y. Cao, G. C. Bazan, J. Am. Chem. Soc. 2006, 128, 14422–14423.
- [5] R. M. Mohareb, M. H. Mohamed, *Heteroat. Chem.* 2001, 12, 518– 527.
- [6] a) K. Hara, M. Kurashige, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, *New J. Chem.* 2003, *27*, 783–785;
 b) Z. S. Wang, Y. Cui, Y. Dan-Oh, C. Kasada, A. Shinpo, K. Hara, *J. Phys. Chem. C* 2007, *111*, 7224–7230; c) Y. M. Cao, Y. Bai, Q. J. Yu, Y. M. Cheng, S. Liu, D. Shi, F. F. Gao, P. Wang, *J. Phys. Chem. C* 2009, *113*, 6290–6297.
- [7] a) J. Fan, H. F. Zhu, T. A. Okamura, W. Y. Sun, W. X. Tang, N. Ueyama, New J. Chem. 2003, 27, 1409–1411; b) S. R. Halper, L. Do,

. 4

www.chemasianj.org

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

RR These are not the final page numbers!

CHEMISTRY AN ASIAN JOURNAL

J. R. Stork, S. M. Cohen, J. Am. Chem. Soc. 2006, 128, 15255–15268;
c) S. S. Li, H. J. Yan, L. J. Wan, H. B. Yang, B. H. Northrop, P. J. Stang, J. Am. Chem. Soc. 2007, 129, 9268–9269;
d) K. Suzuki, M. Kawano, S. Sato, M. Fujita, J. Am. Chem. Soc. 2007, 129, 10652–10653;
e) Y. R. Zheng, H. B. Yang, B. H. Northrop, K. Ghosh, P. J. Stang, Inorg. Chem. 2008, 47, 4706–4711;
f) S. Sato, Y. Ishido, M. Fujita, J. Am. Chem. Soc. 2007, 129, 10652–10653;
e) Y. R. Zheng, H. B. Yang, B. H. Northrop, K. Ghosh, P. J. Stang, Inorg. Chem. 2008, 47, 4706–4711;
f) S. Sato, Y. Ishido, M. Fujita, J. Am. Chem. Soc. 2009, 131, 6064–6065;
g) M. Peterca, M. R. Imam, P. Leowanawat, B. M. Rosen, D. A. Wilson, C. J. Wilson, X. B. Zeng, G. Ungar, P. A. Heiney, V. Percec, J. Am. Chem. Soc. 2010, 132, 11288–11305;
h) Q. F. Sun, J. Iwasa, D. Ogawa, Y. Ishido, S. Sato, T. Ozeki, Y. Sei, K. Yamaguchi, M. Fujita, Science 2010, 328, 1144–1147.

[8] a) S. Sato, J. Iida, K. Suzuki, M. Kawano, T. Ozeki, M. Fujita, *Science* 2006, *313*, 1273–1276; b) T. Kikuchi, S. Sato, M. Fujita, *J. Am. Chem. Soc.* 2010, *132*, 15930–15932.

- [9] M. Ikemi, T. Kikuchi, S. Matsumura, K. Shiba, S. Sato, M. Fujita, *Chem. Sci.* 2010, 1, 68–71.
- [10] N. Kamiya, M. Tominaga, S. Sato, M. Fujita, J. Am. Chem. Soc. 2007, 129, 3816–3817.
- [11] a) K. R. Harris, J. Chem. Phys. 2009, 131, 054503; b) G. Ullmann,
 G. D. J. Phillies, Macromolecules 1983, 16, 1947–1949.
- [12] Gaussian 09, Revision A.1, Frisch et al., Gaussian, Inc., Wallingford CT, 2009.
- [13] M. Tominaga, K. Suzuki, T. Murase, M. Fujita, J. Am. Chem. Soc. 2005, 127, 11950–11951.
- [14] a) H. B. Yang, K. Ghosh, Y. Zhao, B. H. Northrop, M. M. Lyndon, D. C. Muddiman, H. S. White, P. J. Stang, *J. Am. Chem. Soc.* 2008, *130*, 839–841; b) K. Ghosh, J. M. Hu, H. S. White, P. J. Stang, *J. Am. Chem. Soc.* 2009, *131*, 6695–6697.

Received: May 8, 2012 Published online: ■■ ■, 0000

COMMUNICATION

Self-Assembly

Fei Jiang, Ning Wang, Zhengkun Du, Jun Wang, Zhenggang Lan, Renqiang Yang* _____ IIII - IIII

Thiophene-Coated Functionalized M₁₂L₂₄ Spheres: Synthesis, Characterization, and Electrochemical Properties



Instant balls: Well-defined thiophenecoated functional nanospheres were synthesized by instantaneous selfassembly of twelve 90° Pd^{II}-containing compounds and twenty-four 120° organic bidentate ligands in acetone. This solvent system was efficient to prepare the self-assembled complexes, facilitating isolation and purification. The self-assembled functional nanospheres exhibited interesting electrochemical properties.

FR These are not the final page numbers!