## ChemComm

Cite this: Chem. Commun., 2012, 48, 278–280

www.rsc.org/chemcomm

## COMMUNICATION

## Columnar self-assembly of rhomboid macrocyclic molecules *via* step-like intermolecular interaction. Crystal formation and gelation<sup>†</sup>

Tomohito Ide, Daisuke Takeuchi and Kohtaro Osakada\*

Received 26th August 2011, Accepted 3rd November 2011 DOI: 10.1039/c1cc15311k

Two macrocyclic compounds with a rhomboid molecular shape, composed of a  $\pi$ -conjugated framework and an imine or amine functionality, were synthesized. The amine-containing macrocycle crystallizes with step-like interaction of each molecule, forming a columnar arrangement, although dispersion of the imine gelates upon ultrasonification.

Macrocyclic molecules composed of  $\pi$ -conjugated units are expected to have rigid structures and to form a structurally regulated assembly constructed by intermolecular attractive interaction of the arylene, thienylene and alkynylene groups.<sup>1</sup> Stacking of the macrocycle forms its multi-decker type lowdimensional aggregates. Most of such compounds, reported so far, have molecular shapes close to a regular polygon or circle.<sup>2</sup> Macrocyclic  $\pi$ -conjugated molecules with a rhomboid shape also have planar structures but with anisotropic aspects. Although such compounds are much less common, they would form one-dimensional aggregates based on  $\pi$ - $\pi$  stacking, as shown in Fig. 1.<sup>3</sup> In this communication, we report crystal formation and gelation of the rhomboid macrocycles depending on the partial structure and relevance of the molecular structures to the molecular interaction in the assembled structure.

As an extension of our study on the rhomboid macrocycles,<sup>4</sup> we prepared a compound composed of 2,2'-substituted biphenylene and bis(phenylethynyl)benzene units according to the procedure shown in Scheme 1. Macrocycle **1** was prepared by 2:2 cyclocondensation of biphenyl-2,2'-dicarbaldehyde with



**Fig. 1** Illustration of (a) common stacking of a cyclic macrocycle and (b) edge-to-edge stacking of a rhomboid macrocycle.



Scheme 1 Synthetic route of macrocycles. (a) *p*-TsOH, acetonitrile, 0  $^{\circ}$ C, 92%; (b) Zn(Cu), DMF, 0  $^{\circ}$ C, then *p*-TsOH, rt.

1,3-bis(4-aminophenylethynyl)benzene. Intramolecular cyclizative pinacol coupling using Zn(Cu) converts 1 into the cyclic compound 2, containing two *trans*-9,10-diamino-9,10-dihydrophenanthrene groups. The <sup>1</sup>H-NMR, <sup>13</sup>C{<sup>1</sup>H}-NMR, and FAB–MS spectra were consistent with the cyclic structures of 1 and 2, although low solubility of 1 prevented it from  $^{13}C{^{1}H}$ -NMR measurement.

Although attempted recrystallization of 1 was not successful, its molecular structure was optimized by density functional theory computation at the B97-D/TZVP<sup>6,7</sup> level of theory by using Gaussian 09,<sup>8</sup> as shown in Fig. 2(a). The torsion angles between central *m*-phenylene and outer *p*-phenylene groups are 27.5°.

X-Ray crystallography of single crystals of **2** revealed a macrocyclic structure with orthogonal 9,10-diamino-9,10-dihydrophenanthrene units (Fig. 2(b)).<sup>5</sup> The formed six-membered ring has two NH groups with *trans* chemistry. The central *m*-phenylene and two other *p*-phenylene groups are almost

Chemical Resources Laboratory, Tokyo Institute of Technology, 4359 Nagatsuda, Midori-ku, Yokohama 226-8503, Japan. E-mail: kosakada@res.titech.ac.jp; Fax: +81 45-924-5224; Tel: +81 45-924-5224

<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Analytical and spectroscopic characterization for the new compounds and computation details. CCDC 836760. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc15311k



Fig. 2 (a) DFT optimized structure of 1 at the B97-D/TZVP level of theory. (b) Structure of 2 determined by X-ray crystallography. Hydrogen atoms are omitted for clarity.

planar (torsion angle =  $5.5^{\circ}$ ). The dihydrophenanthrene plane is almost perpendicular to the planar macrocycle core. A cyclohexane molecule is included in the cavity of the macrocyclic molecule.

Fig. 3(a) shows packing of the molecules of **2** in the crystal. Two pairs of *p*-phenylene and diphenylethynylene groups in the neighbouring molecules have a short contact with the distance between the centroid of the aromatic ring and the alkynylene of 3.7 Å. This can be ascribed to  $\pi-\pi$  interaction between the ethynylene and phenylene groups. The  $\pi$ - $\pi$  interaction between the aromatic and alkynylene groups is estimated to be more stable than  $\pi - \pi$  interaction between aromatic groups.<sup>9</sup> This interaction forms a step-like linkage of the molecules, and further aggregation of the molecules results in a columnar structure formed by the linearly arranged macrocyclic compounds. A 9,10-dihydrophenanthrene group and a *p*-phenylene group of the molecule contained in the neighbouring columnar assembly have a contact due to CH $-\pi$  interaction with  $d(CH\cdots\pi$  plane) = 2.6 Å, while an aromatic group of the phenanthrene accepts  $CH-\pi$ interaction of the phenylene group of the molecule within the column (2.7 Å). All the columnar assemblies of 2 in the crystals are aligned with the same orientation and have herringbone packing as shown in Fig. 3(b).

The CH- $\pi$  interaction of the 9,10-dihydrophenanthrene group of **2** serves to stabilize attractive interaction between the molecules within the columnar structure and that between a molecule and that in the neighbouring columnar aggregate.

Attempts to crystallize 1 by ultrasonification with organic solvents resulted in formation of its organogel as mentioned below. Ultrasound irradiation of the suspension of 1 (15 mg mL<sup>-1</sup>) in  $CH_2Cl_2$  for 1 min and allowing the mixture to stand for further



**Fig. 3** (a) Intermolecular interaction in the crystal of **2**. The dotted lines denote  $\pi$ - $\pi$  (blue) and CH- $\pi$  interactions (red). (b) Crystal packing of **2**, view along the *a*-axis. Hydrogen atoms and cyclohexanes are omitted for clarity.



Fig. 4 Gelation of macrocycle 1 in CH<sub>2</sub>Cl<sub>2</sub>.



Fig. 5 Optical microscope image ( $\times 2000$ ) of CH<sub>2</sub>Cl<sub>2</sub> gel.

30 min yields opaque gel (Fig. 4). Gelation in DMAc and THF is completed within 1 min and that in DMF requires 20 min. The amount of 1 suited for gel formation in  $CH_2Cl_2$  is within 0.5–8 wt%. Mechanical stirring of 1 in the solvents for 2 days by using a magnetic stirrer or heating of a solid of 1 in DMF (>120 °C) and cooling it to room temperature did not give any gels, but left the original suspension. Hence, this gelation is induced only by ultrasound irradiation.

Fig. 5 shows the optical microscope image of the gel, formed in  $CH_2Cl_2$ , after spreading on a glass plate. It contains fibrous objects with length of several micrometres order and width of submicron order. Therefore, the gels are formed by a network composed of micrometre order fibrous aggregates of **1**.

Drying the gel of 1 *in vacuo* yields its xerogel. Comparison of the SEM (scanning electron microscope) image of 1 before ultrasonification and of its xerogel indicated clear difference of the microstructures, as shown in Fig. 6. The submicron fibrous structures are observed in the xerogel, and have a typical width of  $0.1-0.5 \mu m$ . Therefore, the gels are formed by a network composed of micrometre order fibrous aggregates of 1.



Fig. 6 SEM images and XRD patterns of 1 (a) before ultrasound irradiation, (b) xerogel prepared from  $CH_2Cl_2$  gel.

In addition, IR spectra of 1 before ultrasound irradiation and the xerogel of 1 are almost identical, suggesting that chemical reaction did not occur during the ultrasound irradiation. Powder X-ray diffraction patterns of 1 before the ultrasonification and the xerogels of 1 are included in Fig. 6. Xerogel of 1 exhibits clear diffraction patterns due to the crystalline structure. Maximum of the diffraction intensity was observed at  $2\theta = 23.6^{\circ}$  (d = 3.8 Å) for the CH<sub>2</sub>Cl<sub>2</sub> gel, which may correspond to intermolecular  $\pi$ - $\pi$ stacking in the same manner as macrocycle 2 in the crystal. This result indicated that structurally regulated aggregation via  $\pi$ - $\pi$ stacking between the macrocycles is an important factor in the gelation of 1. Crystals of 2 show a complex diffraction pattern compared with the xerogels, and their major peaks are similar to that of xerogel from CH<sub>2</sub>Cl<sub>2</sub>. The obtained one-dimensional aggregates from CH<sub>2</sub>Cl<sub>2</sub> may have a three-dimensional structure similar to 2.

Sol-gel transition induced by change of temperature and pH as well as photoirradiation was reported. These physical stimuli reorganize interactions such as hydrogen bonds,  $\pi$ - $\pi$  and CH- $\pi$  interactions, and van der Walls interactions between the molecules, forming the network structure suited for gelation.<sup>10</sup> Solution of various compounds and their mixture was reported to form gels upon ultrasonification.<sup>11–16</sup> Most of them are caused by change of conformation of the molecules or of the intermolecular interaction of local functional groups. Macrocycle **1** undergoes ultrasound-induced gelation, and it is based on formation of fibrous aggregates of the molecules during the irradiation.

In summary, macrocycles 1 with twisted biphenyl-2,2'-diimine units and 2 composed of a planar core and orthogonal 9,10dihydrophenanthrene groups at the two acute corners aggregate linearly in the crystals or gel. A rhomboid core composed of *p*-conjugated groups and 9,10-dihydrophenanthrene side group of 2 forms the columnar aggregates and their bundles, as observed by X-ray crystallography. Detailed aggregated structures of 1 are not clear but formation of the fibrous structure, observed in the gels formed by ultrasonification, is attributed to linear aggregation of the molecules *via*  $\pi$ - $\pi$  and CH- $\pi$  interactions.

We thank Dr Daling Lu of the Chemical Resources Laboratory, Tokyo Institute of Technology for SEM measurements. We also thank Prof. Shigeru Machida of Tokyo National College of Technology for optical microscope and photophysical measurements. This work was supported by the Global COE Program "Education and Research Center for Emergence of New Molecular Chemistry". T. I. acknowledges Research Fellowship for Young Scientists from Japan Society for the Promotion of Science.

## Notes and references

- (a) S. Höger, Chem.-Eur. J., 2004, 10, 1320; (b) W. Zhang and J. S. Moore, Angew. Chem., Int. Ed., 2006, 45, 4416; (c) M. Iyoda, Pure Appl. Chem., 2010, 82, 831.
- 2 (a) K. Balakrishnan, A. Datar, W. Zhang, X. Yang, T. Naddo, J. Huang, J. Zuo, M. Yen, J. S. Moore and L. Zang, J. Am. Chem.

Soc., 2006, 128, 6576; (b) K. Nakao, M. Nishimura, T. Tamachi,
Y. Kuwatani, H. Miyasaka, T. Nishinaga and M. Iyoda, J. Am.
Chem. Soc., 2006, 128, 16740; (c) S.-H. Jung, W. Pisula,
A. Rouhanipour, H. J. Räder, J. Jacob and K. Müllen, Angew.
Chem., Int. Ed., 2006, 45, 4685; (d) M. Fritzsche, A. Bohle,
D. Dudenko, U. Baumeister, D. Sebastiani, G. Richardt,
H. W. Spiess, M. R. Hansen and S. Höger, Angew. Chem., Int.
Ed., 2011, 50, 3030.

- 3 (a) H. Kanazawa, M. Higuchi and K. Yamamoto, J. Am. Chem. Soc., 2005, 127, 16404; (b) D. Wang, J. F. Hsu, M. Bagui, V. Dusevich, Y. Wang, Y. Liu, A. J. Holder and Z. Peng, Tetrahedron Lett., 2009, 50, 2147; (c) H. Norouzi-Arasi, W. Pisula, A. Mavrinskiy, X. Feng and K. Müllen, Chem.-Asian J., 2011, 6, 367.
- 4 T. Ide, D. Takeuchi, K. Osakada, T. Sato and M. Higuchi, J. Org. Chem., 2011, 76, 9504.
- 5 Crystal data for **2**:  $C_{90}H_{84}N_42$ : M = 1221.68, monoclinic, space group  $P2_1/n$  (no. 14), a = 9.424(14) Å, b = 17.14(3) Å, c = 23.45(4) Å,  $\beta = 91.541(18)^\circ$ , V = 3786(10) Å<sup>3</sup>, Z = 2,  $D_x = 1.072$ , 31070 reflections measured, 8020 unique reflections, 1709 observations ( $I > 2.0\sigma(I)$ ), R = 0.1181 ( $I > 2.0\sigma(I)$ ),  $R_w = 0.2957$  ( $I > 2.0\sigma(I)$ ). CCDC 836760. Low quality of the crystals hindered discussion of detailed bond parameters of the compound.
- 6 S. Grimme, J. Comput. Chem., 2006, 27, 1787.
- 7 A. Schäfer, C. Huber and R. Ahlrichs, J. Chem. Phys., 1994, 100, 5829.
- 8 M. J. Frisch, et al., Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010. A full reference may be found in ESI<sup>†</sup>.
- 9 Interaction energy of the benzene–diphenylethyne π–π complex is -18.3 kJ mol<sup>-1</sup> and the benzene–benzene parallel-displaced stacking π–π complex is -11.2 kJ mol<sup>-1</sup> at the B97-D/TZVP level of theory.
- 10 (a) T. Saji, K. Hoshino, Y. Ishii and M. Goto, J. Am. Chem. Soc., 1991, **113**, 450; (b) K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Ohseto, K. Ueda and S. Shinkai, J. Am. Chem. Soc., 1994, **116**, 6664; (c) L. Frkanec, M. Jokić, J. Makarević, K. Wolsperger and M. Žinić, J. Am. Chem. Soc., 2002, **124**, 9716; (d) K. J. C. van Bommel, C. van der Pol, I. Muizebelt, A. Friggeri, A. Heeres, A. Meetsma, B. L. Feringa and J. van Esch, Angew. Chem., Int. Ed., 2004, **43**, 1663; (e) K. Tsuchiya, Y. Orihara, Y. Kondo, N. Yoshino, T. Ohkubo, H. Sakai and M. Abe, J. Am. Chem. Soc., 2004, **126**, 12282; (f) M. Yamanaka, N. Haraya and S. Yamamichi, Chem.-Asian J., 2011, **6**, 1022.
- (a) Y. Li, T. Wang and M. Liu, *Tetrahedron*, 2007, 63, 7468;
  (b) K. Isozaki, H. Takaya and T. Naota, *Angew. Chem., Int. Ed.*, 2007, 46, 2855;
  (c) D. Bardelang, F. Camerel, J. C. Margeson, D. M. Leek, M. Schmutz, M. B. Zaman, K. Yu, D. V. Soldatov, R. Ziessel, C. I. Ratcliffe and J. A. Ripmeester, *J. Am. Chem. Soc.*, 2008, 130, 3313;
  (d) J. Wu, T. Yi, T. Shu, M. Yu, Z. Zhou, M. Xu, Y. Zhou, H. Zhang, J. Han, F. Li and C. Huang, *Angew. Chem., Int. Ed.*, 2008, 47, 1063.
- 12 (a) C. Wang, D. Zhang and D. Zhu, J. Am. Chem. Soc., 2005,
  127, 16372; (b) M. Yamanaka, T. Nakamura, T. Nakagawa and H. Itagaki, *Tetrahedron Lett.*, 2007, 48, 8990; (c) C. Baddeley,
  Z. Yan, G. King, P. M. Woodward and J. D. Badjić, J. Org. Chem., 2007, 72, 7270; (d) S. M. Park and B. H. Kim, Soft Matter, 2008, 4, 1995.
- 13 Y. Wang, C. Zhan, H. Fu, X. Li, X. Sheng, Y. Zhao, D. Xiao, Y. Ma, J. S. Ma and J. Yao, *Langmuir*, 2008, 24, 7635.
- 14 (a) Y. He, Z. Bian, C. Kang, R. Jin and L. Gao, New J. Chem., 2009, **33**, 2073; (b) X. Chen, Z. Huang, S.-Y. Chen, K. Li, X.-Q. Yu and L. Pu, J. Am. Chem. Soc., 2010, **132**, 7297.
- (a) T. Naota and H. Koori, J. Am. Chem. Soc., 2005, 127, 9324;
  (b) S. Zhang, S. Yang, J. Lan, Y. Tang, Y. Xue and J. You, J. Am. Chem. Soc., 2009, 131, 1689.
- 16 K. M. Anderson, G. M. Day, M. J. Paterson, P. Byrne, N. Clarke and J. W. Steed, *Angew. Chem., Int. Ed.*, 2008, **47**, 1058.