Organic Letters

Letter

pubs.acs.org/OrgLett

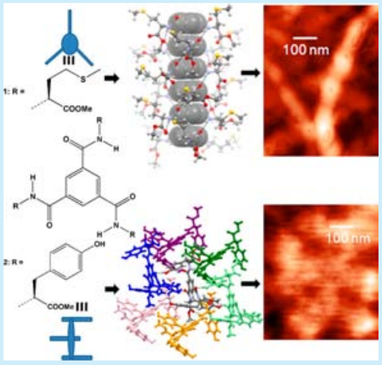
Porous Organic Material from Discotic Tricarboxyamide: Side Chain–Core interactions

Poulami Jana, Arpita Paikar, Santu Bera, Suman Kumar Maity, and Debasish Haldar*

Department of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur, West Bengal 741252, India

S Supporting Information

ABSTRACT: The benzene-1,3,5-tricarboxyamide containing three L-methionine (**1**) self-assemble through 3-fold amide–amide hydrogen bonds and π–π stacking to fabricate one-dimensional nanorod like structure. However, the tyrosine analogue (**2**) carrying multiple H-bonding side chains lost the C_3 symmetry and 3-fold amide–amide hydrogen bonds and developed a porous structure. The porous material exhibits ten times more N_2 sorption (155 cc/g) than the columnar one, indicating that side chain–core interactions have a drastic effect on structure and function.



The organization of building blocks in a particular fashion is the key step toward the fabrication of new materials and devices.[1] The organized materials are developed by association of the cooperative building blocks through H-bonding, metal–ion complexation, electrostatic interactions, and hydrophobic interactions. The numbers of such organized materials by assembly of synthetic building blocks are growing.[2]

Over the past decades, large numbers of discotic building blocks with a wide range of amplified properties have been heavily studied.[3] A broad range of discotic benzene-1,3,5-tricarboxyamides have been synthesized and studied in detail.[2e] Various functional groups such as alkyl,[4] aryl,[5] pyridyl,[6] bipyridyl,[7] porphyrinyl,[8] triphenylyl,[9] oligo(*p*-phenylenevinylene),[10] amino acid,[11] dipeptide,[12] oligopeptide,[13] oligo(ethyleneoxy),[14] and benzocrown ethers[15] have been incorporated in the tricarboxyamide. The tricarboxyamides may be chiral nonracemic, racemic, or achiral. When three identical functional groups are connected to the amides, the tricarboxyamides are C_3 symmetric. These tricarboxyamide derivatives have wide applications such as organogels,[16] hydrogels,[17] liquid crystals,[18] nanostructured materials,[19] MRI contrast reagents,[20] nucleating agents for polymers,[21] metal complexation reagents,[11d] and microcapsules for drug delivery.[22] Until now, studies on tricarboxyamides have focused on the aggregations by core–core interactions and 3-fold amide–amide hydrogen bonding. However, the report on the effect of side chain–core interactions on the self-assembly of discotic tricarboxyamides is rare.[2e]

Here, we describe an example of very unusual nonhelical assembly from discotic tricarboxyamides at the atomic level. Specifically, we show that the side-chain–core interactions have a significant effect on self-assembly of chiral benzene-1,3,5-tricarboxyamide. However, the tricarboxyamide possesses the remarkable ability to form columnar superstructures consisting of cofacially stacked π face in its interior, while its exterior is surrounded by a hydrocarbon wrapper. The reported tyrosine-containing chiral tricarboxyamide **2** adopts nanoporous structures.

For tricarboxyamides **1** and **2** the design principle explored was how to use the chiral amino acid side chains to force the amides functional groups out of the plane of the central aromatic ring and adopt a conformation that facilitates formation of three intermolecular hydrogen bonds. For tricarboxyamide **2**, we used the Tyr residue to introduce additional hydrogen bonds and steric hindrence. Target compounds **1** and **2** were synthesized by functionalizing benzene-1,3,5-tricarboxylic acid with the appropriate chiral amino acid methyl ester following a high purity, as confirmed by ^1H NMR, ^{13}C NMR, FTIR, and mass spectrometry (MS) analysis.

The self-assembly of the reported discotic compounds **1** and **2** containing chiral side chains has been studied using a wide variety of different spectroscopic techniques in dilute methanol. From solution-state studies, the UV–vis spectroscopy of tricarboxyamides **1** and **2** in methanol shows a bathochromic shift of the absorption maximum with increasing concentration (Figure 1). Circular dichroism (CD) spectroscopy of discotic compound **1** in dilute methanol solutions indeed shows a strong Cotton effect centered around 218 nm, confirming the helical nature of the aggregates (Figure 1, Supporting Information).[23] Further analysis reveals that the tricarboxya-

Received: October 4, 2013
Published: December 18, 2013

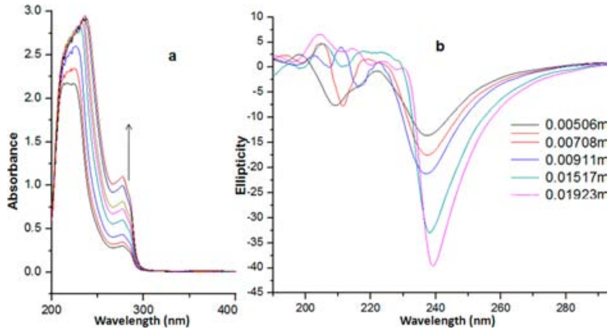


Figure 1. (a) UV−vis absorption spectra of the tricarboxyamide **2** at different concentrations in methanol. (b) CD spectra of **2** at different concentrations in methanol.

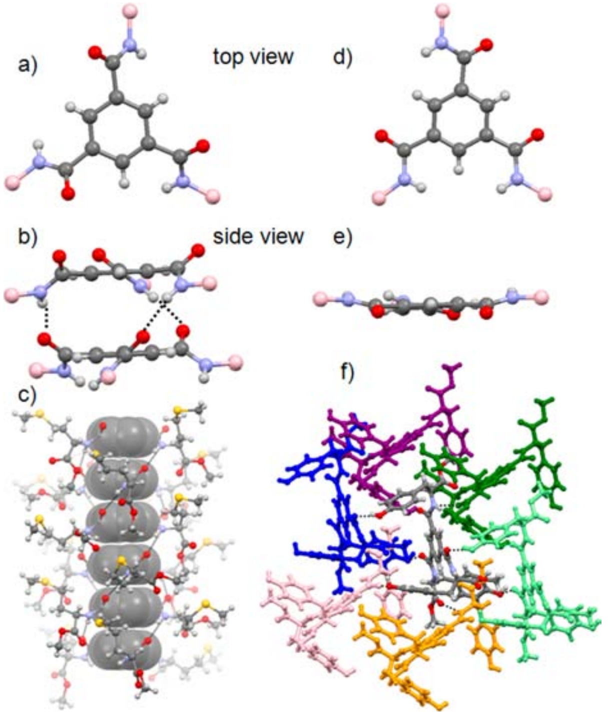


Figure 2. (a, b) Top and side view of tricarboxyamide **1** with intermolecular hydrogen bonds in the solid state. (c) Columnar assembly through multiple intermolecular N−H···O hydrogen bonds and $\pi-\pi$ stacking interactions of **1**. (d, e) Solid state molecular structures of tricarboxyamide **2**. (f) Cagelike packing of **2** in the solid state by multiple intermolecular N−H···O and O−H···O hydrogen-bonding interactions. Hydrogen bonds are shown as dotted lines. In (a), (b), (d), and (e), amino acid side chains, α-hydrogens, and acid groups have been removed to clarify the view.

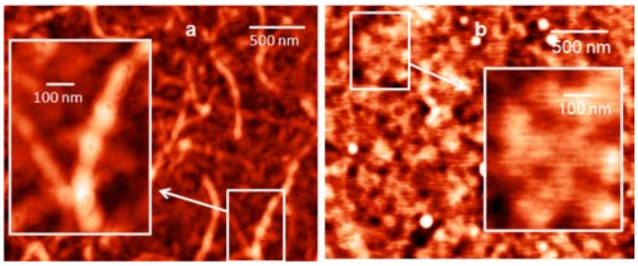


Figure 3. AFM image of tricarboxyamide **1** showing helical nano fibers. (b) AFM image showing polydisperse nanoporous morphology of tricarboxyamide **2**.

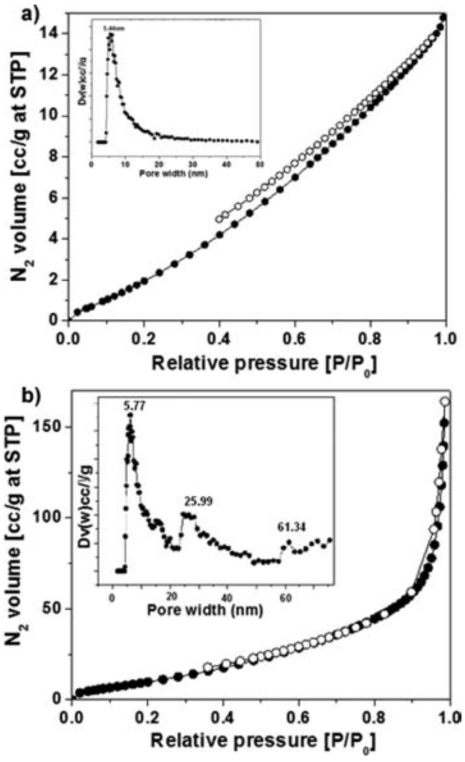


Figure 4. N_2 sorption isotherm of (a) tricarboxyamide **1** and (b) tricarboxyamide **2** at 77 K (P_0 = 1 atm). Black circle: sorption. White circle: desorption.

mide **2** in dilute methanol solutions shows strong Cotton effects around 210 and 237 nm. However, with increasing concentration the peak at 210 nm disappeared and intensity of 237 nm peak increased. The results indicate that the self-assembly pattern of tricarboxyamide **2** is significantly different from that of **1**.

Further, the solid state FT-IR spectroscopy has been used to investigate the self-assembly and arrangement of the intermolecular H-bonding of tricarboxyamides. FT-IR spectra of methionine substituted symmetric discotic compound **1** gave rise to typical NH, amide I and amide II vibrations at 3231, 1641, and 1555 cm^{-1} confirming the presence of 3-fold intermolecular H-bonding (Figure 2, Supporting Information). These results indicate that the presence of methionine side chains next to the amide core does not affect the H-bonding pattern in discotic tricarboxyamide **1**. For more polar tyrosine substituted discotic tricarboxyamide **2**, the H-bonding pattern changes in the solid state as evidenced by FT-IR spectroscopy. The N−H stretch appears at 3378 cm^{-1} and C═O stretch at 1656 cm^{-1} suggesting the loss of 3-fold intermolecular H-bonding (Figure 3, Supporting Information).[24] This result indicates a lack of columnar order in compound **2** at room temperature. Meijer and co-workers have reported the presence of 3-fold intermolecular H-bonding in phenylalanine substituted symmetric discotic compound by the solid state FT-IR spectroscopy and concluded that the presence of bulky benzyl groups next to the amide core does not necessarily affect the H-bonding pattern.[11e] Hence, lack of columnar order in tricarboxyamide **2** may be attributed to competitive intermolecular H-bonding between tyrosine phenolic oxygen and amide hydrogen of the tricarboxyamide core.

Finally, X-ray crystallography sheds some light on molecular structures and self-assembly pattern of the chiral tricarboxyamides **1** and **2**. Colorless hexagonal crystals of compound **1** and colorless monoclinic crystals of compound **2** suitable for X-ray diffraction studies were obtained from their respective methanol−water solutions by slow evaporation.[25] Shown in Figure 2a is the crystal structure of compound **1**. From the crystal structure, the amide groups are out of the central ring plane and Met side chains are in same face of compound **1**. However, aromatic amides prefer coplanarity[26] of the carbonyl functional group with the aryl system to optimize conjugation, in compound **1** the amides are tilted toward the same direction. This is because of the competition between the demand of conjugation (amide and aryl) and that of intermolecular NH···O═C H-bonding. Hence the crystal structure of discotic compound **1** showed 3-fold intermolecular H-bonding.[27] The center-to-center distance between the benzene rings in columnar assembly is about 3.35 Å. The amide twist angle (38.5°, 41.8,° and 42.4°) out of the central benzene ring plane modulates the distance between adjacent molecules. From Figure 2b, each molecule of **1** has a permanent dipole moment. The direction of the dipole moment is perpendicular to the central benzene ring plane. Hence in the columnar stacking the dipoles could sum to generate a macroscopic dipole moment. The torsion angles (ω, ϕ, ψ) around the methionine residues appears to play a critical role in dictating the overall structural features and columnar stacking of **1**. The helical columnar assemblies are further stabilizing by three cooperative hydrogen bonding interactions of amide groups (Figure 2c) (Table, 1, Supporting Information). For **1**, in higher order assembly, a honeycomb-like structure has been observed (Figure 4, Supporting Information). From the solid-state structure of discotic compound **2**, the amide groups are almost in the same plane of the central benzene ring though the molecule contains sterically hindered tyrosines (Figure 2d,e).The three amides make torsion angles of 17.6°, 18.7°, and 162.2° with the aryl mean plane. The solid state structure of **2** exhibits that the two tyrosine side chains are in the same face and the third one is in the opposite face of the central benzene ring (Figure 5, Supporting Information). The crystal structure of discotic triacrboxyamide **2** showed no 3-fold intermolecular NH···O═C hydrogen bonding and the loss of C_3 symmetry.

The steric hindrance and competitive intermolecular H-bonding between side chains and tricarboxyamide core appear to play a critical role in dictating the overall structural features of **2**. Moreover, each molecule of compound **2** interacts with six surrounding molecules through multiple N−H···O and O−H···O intermolecular hydrogen bonds between tyrosine phenolic oxygen and amide hydrogen of the tricarboxyamide core and developed a porous structure in higher order assembly (Figure 2f).

The analysis of the morphology of compound **1** by atomic force microscopy (AFM) reveals the formation of fibers have diameter c.a. 100 nm and several micrometer in length (Figure 3a). The compound **1** shows spontaneous nucleation, interfacial control, and one-dimensional growth which results in the molecules stacking into fibers. However, the AFM images of tricarboxyamide **2** show polydisperse nanoporous morphology (Figure 3b). The loss of C_3 symmetry and 3-fold intermolecular amide−amide hydrogen bonding have promoted the phenolic oxygen and core hydrogen bonds and cluster formation.

In order to examine the porous structure, gas absorption studies have been performed. Tricarboxyamide **1** exhibits a type-III N_2 sorption isotherm (Figure 4a). The pore size in compound **1** is 5.44 nm and N_2 uptake was 14.99 cc/g. The N_2 sorption studies with evacuated sample of compound **2** exhibit a type-I isotherm (Figure 4b). The pore size distribution curve of compound **2** showed three peaks at 5.77, 25.99, and 61.34 nm indicating a polydisperse nanoporous structure. The N_2 uptake of compound **2** was found to be 155 cc/g. Hence the unusual packing of compound 2 helps to adsorb N_2 ten times more than that of compound **1**. The PXRD spectra of **2** used for gas sorption experiment (Figure 6a, Supporting Information) and the powder pattern from X-ray crystallography (Figure 6b, Supporting Information) of **2** confirmed the existence of same structure in both.

In summary, the atomic level analysis reveals that benzene-1,3,5-tricarboxyamide-containing methionine faciliates formation of the cofacially stacked columnar structure but the tyrosine analogue self-assembles to form nanoporous material. The tricarboxyamide **2** exhibits 10 times higher N_2 sorption than **1**. These findings indicate that the side chain−core interactions have drastic effects on structure and function. Further studies on these compounds should reveal additional novelties.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, spectral characterization, and crystallographic data for **1** and **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: deba_h76@yahoo.com.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge the CSIR, New Delhi, India (Project No 01/2507/11-EMR-II). P.J. and S.K.M. thank CSIR, India, for fellowships. A.P. and S.B. thank UGC, India, for fellowship.

■ REFERENCES

(1) (a) Lehn, J. M. *Supramolecular Chemistry*; VCH: Weinheim, 1995. (b) Mastalerz, M.; Oppel, I. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 5252. (c) Mastalerz, M. *Chem.—Eur. J.* **2012**, *18*, 10082.

(2) (a) Hecht, V.; Huc, I. *Foldamer*; Wiley-VCH: Weinheim, 2007. (b) Nagai, A.; Chen, X.; Feng, X.; Ding, X.; Guo, Z.; Jiang, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 3770. (c) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. *Chem. Rev.* **2005**, *105*, 1491. (d) Zayed, J. M.; Nouvel, N.; Rauwald, U.; Scherman, O. A. *Chem. Soc. Rev.* **2010**, *39*, 2806. (e) Cantekin, S.; Greef, T. F. A.; Palmans, A. R. A. *Chem. Soc. Rev.* **2012**, *41*, 6125.

(3) Bushey, M. L.; Nguyen, T. Q.; Zhang, W.; Horoszewski, D.; Nuckolls, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 5446.

(4) (a) Matsunaga, Y.; Miyajima, N.; Nakayasu, Y.; Sakai, S.; Yonenaga, M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 207. (b) Stals, P. J. M.; Everts, J.; de Bruijn, R.; Filot, I. A. W.; Smulders, M. M. J.; Martín-Rapú n, R.; Pidko, E. A.; de Greef, T. F. A.; Palmans, A. R. A.; Meijer, E. W. *Chem.—Eur. J.* **2010**, *16*, 810.

(5) (a) van Gorp, J. J.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **2002**, *124*, 14759. (b) Bernet, A.; Albuquerque, R. Q.; Behr, M.; Hoffmann, S. T.; Schmidt, H.-W. *Soft Matter.* **2012**, *8*, 66.

(6) Palmans, A. R. A.; Vekemans, J. A. J. M.; Meijer, E. W.; Kooijmans, H.; Spek, A. L. *Chem. Commun.* **1997**, 2247.

(7) Brunsveld, L.; Zhang, H.; Glasbeek, M.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 6175.

(8) van Hameren, R.; Schön, P.; van Buul, A. M.; Hoogboom, J.; Lazarenko, S. V.; Gerritsen, J. W.; Engelkamp, H.; Christianen, P. M.; Heus, H. A.; Maan, J. C.; Rasing, T.; Speller, S.; Rowan, A. E.; Elemans, J. A. A. W.; Nolte, R. J. M. *Science* **2006**, *314*, 1433.

(9) Paraschiv, I.; Giesbers, M.; van Lagen, B.; Grozema, F. C.; Abellon, R. D.; Siebbeles, L. D. A.; Marcelis, A. T. M.; Zuilhof, H.; Sudhölter, E. J. R. *Chem. Mater.* **2006**, *18*, 968.

(10) van Herrikhuyzen, J.; Jonkheijm, P.; Schenning, A. P. H. J.; Meijer, E. W. *Org. Biomol. Chem.* **2006**, *4*, 1539.

(11) (a) de Loos, M.; van Esch, J. H.; Kellogg, R. M.; Feringa, B. L. *Tetrahedron* **2007**, *63*, 7285. (b) Bose, P. P.; Drew, M. G. B.; Das, A. K.; Banerjee, A. *Chem. Commun.* **2006**, 3196. (c) Besenius, P.; Portale, G.; Bomans, P. H. H.; Janssen, H. M.; Palmans, A. R. A.; Meijer, E. W. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 17888. (d) Gelinsky, M.; Vogler, R.; Vahrenkamp, H. *Inorg. Chem.* **2002**, *41*, 2560. (e) Veld, M. A. J.; Haveman, D.; Palmans, A. R. A.; Meijer, E. W. *Soft Matter* **2011**, *7*, 524.

(12) Hout, K. P. v. d.; Martín-Rapún, R.; Vekemans, J. A. J. M.; Meijer, E. W. *Chem.—Eur. J.* **2007**, *13*, 8111.

(13) Matsuura, K.; Murasato, K.; Kimisuka, N. *J. Am. Chem. Soc.* **2005**, *127*, 10148.

(14) Stals, P. J. M.; Haveman, J. F.; Martín-Rapún, R.; Fitié, C. F. C.; Palmans, A. R. A.; Meijer, E. W. *J. Mater. Chem.* **2009**, *19*, 124.

(15) Lee, S.; Lee, J.-S.; Lee, C. H.; Jung, Y.-S.; Kim, J.-M. *Langmuir* **2011**, *27*, 1560.

(16) Shikata, T.; Ogata, D.; Hanabusa, K. *J. Phys. Chem. B* **2004**, *108*, 508.

(17) Shi, N.; Dong, H.; Yin, G.; Xu, Z.; Li, S. *Adv. Funct. Mater.* **2007**, *17*, 1837.

(18) Matsunaga, Y.; Miyajima, N.; Nakayasu, Y.; Sakai, S.; Yonenaga, M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 207.

(19) Fitié, C. F. C.; Tomatsu, I.; Byelov, D.; de Jeu, W. H.; Sijbesma, R. P. *Chem. Mater.* **2008**, *20*, 2394.

(20) Besenius, P.; Heynens, J. L. M.; Straathof, R.; Nieuwenhuizen, M. M. L.; Bomans, P. H. H.; Terreno, E.; Aime, S.; Strijkers, G. J.; Nicolay, K.; Meijer, E. W. *Contrast Media Mol. Imaging* **2012**, *7*, 356.

(21) Blomenhofer, M.; Ganzleben, S.; Hanft, D.; Schmidt, H.-W.; Kristiansen, M.; Smith, P.; Stoll, K.; Maeder, D.; Hoffmann, K. *Macromolecules* **2005**, *38*, 3688.

(22) Broaders, K. E.; Pastine, S. J.; Grandhe, S.; Fréchet, J. M. J. *Chem. Commun.* **2011**, *47*, 665.

(23) Brunsveld, L.; Schenning, A. P. H. J.; Broeren, M. A. C.; Janssen, H. M.; Vekemans, J. A. J. M.; Meijer, E. W. *Chem. Lett.* **2000**, 292.

(24) Stals, P. J. M.; Smulders, M. M. J.; Martín-Rapún, R.; Palmans, A. R. A.; Meijer, E. W. *Chem.—Eur. J.* **2009**, *15*, 2071.

(25) Crystallographic data: Compound **1**: $C_{27}H_{39}N_3O_9S_3$, M_w = 645.82, hexagonal, space group $P65$, a = 16.4549(12) Å, b = 16.4549(12) Å, c = 21.286(3) Å, V = 4991.3 (9)Å^3, Z = 6, dm = 1.289 Mg m^{-3}, K = 100, R1 0.0780 and wR2 0.2483 for 5031data with $I > 2\sigma(I)$. Compound **2**: $C_{39}H_{39}N_3O_{12}$, M_w = 741.73, monoclinic, space group $P2_1$, a = 9.122(2) Å, b = 16.331(4) Å, c = 12.941(3) Å, V = 1833.3 (8)Å^3, Z = 2, dm = 1.344 Mg m^{-3}, K = 100, R1 0.0477 and wR2 0.1094 for 6341 data with $I > 2\sigma(I)$. Intensity data were collected with MoKα radiation for compounds **1** and **2** using Bruker APEX-2 CCD diffractometer. Data were processed using the Bruker SAINT package and the structure solution and refinement procedures were performed using SHELX97. The non-hydrogen atoms were refined with anisotropic thermal parameters. The data have been deposited at the CCDC with reference number CCDC 884523 and 884524, respectively.

(26) Konig, B.; Moller, O.; Bubenitschek, P.; Jones, P. G. *J. Org. Chem.* **1995**, *60*, 4291.

(27) Rajput, L.; Biradha, K. *J. Mol. Struct.* **2008**, *876*, 339.