(Revised 07/09)

RGC Ref.: N_CUHK467/10 NSFC Ref. : 21061160494
(please insert ref. above)

NSFC/RGC Joint Research Scheme
Joint Completion Report

(Please attach a copy of the completion report submitted to the NSFC by the Mainland researcher)

Part A: The Project and Investigator(s)

1. Project Title Supramolecular Assembly of Novel Tribenzotriquinacene (TBTQ) Derivatives

2. Investigator(s) and Academic Department/Units Involved

	Hong Kong Team	Mainland Team
Name of Principal Investigator *(with title)*	Hak-Fun Chow, Dr.	Xiao-Ping Cao, Dr.
Post	Professor	Professor
Unit / Department / Institution	Chemistry/CUHK	Chemistry/Lanzhou University
Co-investigator(s) *(with title)*		Dietmar Kuck, Prof. Dr.

3. Project Duration

	Original	Revised	Date of RGC/ Institution Approval *(must be quoted)*
Project Start date	1 Jan 2011		
Project Completion date	31 Dec 2013		
Duration *(in month)*	36		

Part B: The Completion Report

5. Project Objectives

5.1 Objectives as per original application

1. To develop new synthetic routes to various hydrogen bonding or metal ligating functional tribenzotriquinacene (TBTQ) derivatives
2. To study and characterize the structures of the resulting self-assembling products
3. To examine the host-guest complexation properties, if any, of the above assemblies

5.2 Revised Objectives

Date of approval from the RGC: NA

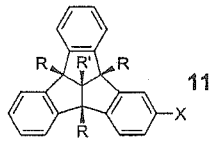
Reasons for the change: NA

6. Research Outcome

Major findings and research outcome
(maximum 1 page; please make reference to Part C where necessary)

(Revised 07/09)

1. In order to prepare supramolecular self-assemblies based on the TBTQ skeleton, it was necessary to develop highly regio- and enantio-selective preparative routes towards the 2,6-disubstituted **12** and 2,6,10-trisubstituted derivatives **13**. Due to the orthogonal disposition of the functionalities, compounds **12** and **13** are candidates for the construction of molecular squares and cubes, respectively. Despite many problems (poor solubility property of the TBTQ compounds, low product yield of the synthetic routes, tedious purification of TBTQ regioisomers *etc.*) encountered in this project, we were finally able to secure a relatively reliable route to synthesize optically pure 2-monosubstituted **11**, 2,6-disubstituted **12** and 2,6,10-trisubstituted **13** compounds in a highly regioselective manner by modification of the original procedures reported by Kuck (the co-investigator of this project) and Hopf (an independent investigator). This research outcome had been accepted for publication in *The Journal of Organic Chemistry*. The result of this work was also presented at the 26th International Symposium on Chiral Discrimination in Prague in 2014.



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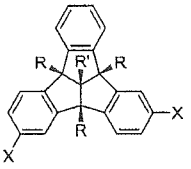
R = Pr; R' = Me; X = OH
R = H; R' = H; X = OMe



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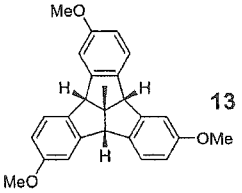
R = Pr; R' = Me; X = OH
R = H; R' = H; X = OMe



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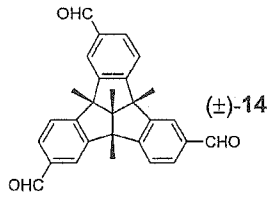
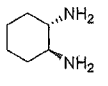
2. Several strategies were employed to construct supramolecular assemblies based on the above TBTQ derivatives. First we examined the dynamic covalent chemistry between the racemic 2,6,10-trialdehyde **14** with optically pure 1*S*,2*S*-diaminocyclohexane **15**, which resulted in the formation of the three diastereomeric cryptophanes **5**–**7** that possess a large internal cavity in high yields. The outcome of the research was published in *The Journal of Organic Chemistry* in 2013 and also presented at the *The 7th International Conference on Cutting-Edge Organic Chemistry in Asia* in 2012. We also examined the hydrogen-bond mediated self-assembly of the racemic 2,6,10-trimethanol (±)-**16**, and found that this compound formed nanotubes in the crystalline state. We also investigated the use of metal-ligation to form self-assembled molecular square **9** from an optically pure 2,6-disubstituted TBTQ derivative **17**. Right now the dimeric compound **8** was successfully synthesized and we are just two steps away from securing the target molecule **9**. As a result of these research findings, it can be concluded that such TBTQ derivatives do possess unique molecular architecture to enable them to construct supramolecular assemblies easily.



(±)-**14**



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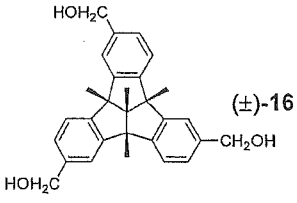
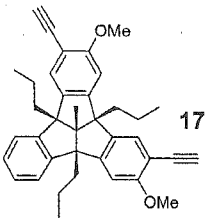


(±)-**16**



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3. We also examined the host guest chemistry of some of the TBTQ derivatives. Of particular interest was the finding that the nanotube formed from the racemic 2,6,10-trimethanol (±)-**16** could encapsulate solvent molecules. The outcome of this work was published simultaneously in the above-mentioned *The Journal of Organic Chemistry* in 2013. It was also shown that several benzofurano-annelated TBTQ hosts (*e.g.* **10**) could act as hosts for C_{60} fullerene.

4. Three PhD students undertook this project. One (Wang) already obtained his PhD in Lanzhou University in 2012. The other two students are still pursuing their PhD study at CUHK. One (Xu) is expected to complete her study in Aug 2015, and the other (Ip) in Aug 2017.

Potential for further development of the research and the proposed course of action *(maximum half a page)*

As we have shown in sections 5 and 6, there are enormous potentials and opportunities to further develop the supramolecular chemistry of 2,6-disubstituted **2** and 2,6,10-trisubstituted **3** TBTQ compounds. It was impossible to exhaust all these possibilities within the three-year working time-frame of this project, given that we initially faced some unexpected problems when developing viable synthetic routes to these molecular modules. Work will be continued on this project on the following issues:

1. To complete the synthesis of the molecular square **9** and to examine its host-guest complexation properties, given that the host now has a much bigger cavity.
2. To prepare molecular cubes based on the 2,6,10-trisubstituted TBTQ derivatives **3** via metal-ligation or hydrogen bonding interaction.
3. To append fused aromatic or graphene units into the TBTQ molecules so as to create non-planar graphene sheets which may possess interesting optical and electronic properties.

7. The Layman's Summary

(describe in layman's language the nature, significance and value of the research project, in no more than 200 words)

This project seeks to develop novel molecular materials from a special class of molecules called tribenzotriquinacenes (TBTQs). Due to their unique three-dimensional geometry, they can be used readily to prepare fascinating nanoscopic molecular objects such molecular cages. It was found that this kind of materials can trap small molecules in their internal cavities and therefore can have potential applications in separation technology and drug delivery.

Part C: Research Output

8. Peer-reviewed journal publication(s) arising directly from this research project

(Please attach a copy of each publication and/or the letter of acceptance if not yet submitted in the previous progress report(s). All listed publications must acknowledge RGC's funding support by quoting the specific grant reference.))

The Latest Status of Publications				Author(s) *(bold the authors belonging to the project teams and denote the corresponding author with an asterisk*)*	Title and Journal/Book *(with the volume, pages and other necessary publishing details specified)*	Submitted to RGC *(indicate the year ending of the relevant progress report)*	Attached to this report *(Yes or No)*	Acknowledged the support of this Joint Research Scheme *(Yes or No)*
Year of publication	Year of Acceptance *(For paper accepted but not yet published)*	Under Review	Under Preparation *(optional)*					

2013				Wang, T.; Zhang, Y.-F.; Hou, Q.-Q.; Xu, W.-R.; **Cao, X.-P.***; **Chow, H.-F.,* Kuck, D.***	*C*3-Symmmetrical tribenzotriquinacene derivatives: Optical resolution through cryptophane synthesis and supramolecuar self-assembly into nanotubes, *J. Org. Chem.* **2013**, *78*, 1062–1069.		Yes	Yes
2014	2014			Xu, W.-R.; **Chow, H.-F.,* Cao, X.-P.*; Kuck, D.***	Regiocontrolled synthesis and optical resolution of mono-, di- and tri-substituted tribenzotriquinacene derivatives – Key building blocks for further assembly into molecular squares and cubes, *J. Org. Chem.*, accepted for publication.		Yes	Yes

9. Recognized International conference(s) in which paper(s) related to this research project was/were delivered *(Please attach a copy of each delivered paper)*

Month/Year/ Place	Title	Conference Name	Submitted to RGC *(indicate the year ending of the relevant progress report)*	Attached to this report *(Yes or No)*	Acknowledged the support of this Joint Research Scheme *(Yes or No)*
Dec/2012/Singapore	Supramolecular Chemistry of Tribenzotriquinacene Derivatives	The 7th International Conference on Cutting-Edge Organic Chemistry in Asia		Yes	Yes
Jul/2014/Prague	Synthesis and Optical Resolutions of Tribenzotriquinacene Derivatives	Chirality 2014 (26th International Symposium on Chiral Discrimination)		Yes	Yes

10. Student(s) trained *(Please attach a copy of the title page of the thesis.)*

Name	Degree registered for	Date of registration	Date of thesis submission/ graduation
Tao Wang	PhD, Lanzhou University	1 Sep 2006	1 May 2012
Wenrong Xu	PhD, CUHK	1 Aug 2011	31 Jul 2015
Ho-Wang Ip	PhD, CUHK	1 Aug 2013	31 Jul 2017

11. Other impact *(e.g. award of patents or prizes, collaboration with other research institutions, technology transfer, etc.)*

It has been a pleasure to collaborate with Prof. Dietmar Kuck of the University of Bielefeld of Germany.