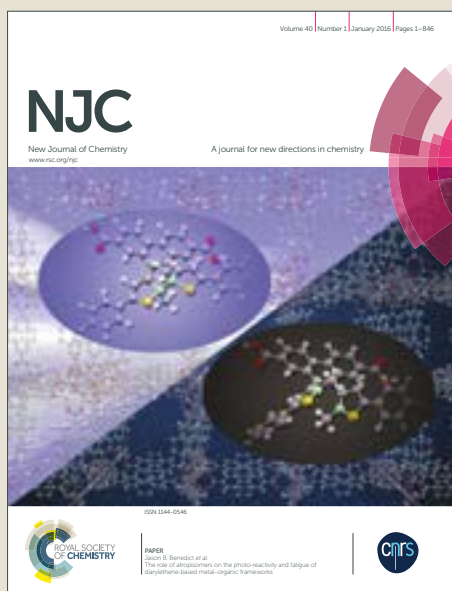


NJC

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: C. Yu, Y. Chen and C. Wang, *New J. Chem.*, 2017, DOI: 10.1039/C7NJ02735D.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

Synthesis and Ring Opening Reaction of Octaoctyl Substituted [2.2.2.2](2,7)-Fluorenophanetetraene by Photooxidation

Chin-Yang Yu*, Yu-Chi Chen and Chao-Chi Wang

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

Octaoctyl substituted fluorenophanetetraene has been synthesized from their corresponding octaoctyl substituted tetrathia[3.3.3.3]fluorenophanes followed by benzyne Stevens rearrangement, oxidation and thermal elimination. The solid-state structure of octaoctyl substituted [2.2.2.2](2,7)-fluorenophanetetraene reveals that the fluorene units connect by *cis* vinylenes and alkyl chains locate inside and outside the rings. The photooxidation reaction of the fluorenophanetetraene was carried out in dilute solution under UV light irradiation to give all *trans* linear fluorenevinylene with aldehyde end groups. The optical properties of fluorenophanetetraene and its linear compound generated by photooxidation have been investigated and compared. The fluorescence quantum yield of fluorenophanetetraene in solution is much lower than its linear compound generated by photooxidation due to the shorter effective conjugation lengths, however, the fluorescence intensity of fluorenophanetetraene in the solid state is much higher than that of its linear compound generated by photooxidation possibly due to the weak intermolecular interaction.

Introduction

Cyclic conjugated molecules are one of the most promising materials in the field of optoelectronic applications.^[1] Cyclophanes and their derivatives, in particular those containing aromatic rings linked by *cis*-vinylenes have attracted much attention for more than five decades due to their ring strain and unusual intramolecular π - π stacking structures and the unique optical and electronic properties^[2] in comparison with those of linear analogues. A number of recent reports on the preparation of alkoxy substituted phenylenevinylene homopolymers and block copolymers have demonstrated that the microstructures, molecular weights, polydispersity and end groups of the polymers can be controlled by ring opening metathesis polymerization of alkoxy substituted cyclophanediene and cyclophanetriene derivatives using Grubbs ruthenium carbene initiator.^[3] These conjugated polymers have been intensively used in light emitting diodes, chemosensors, photovoltaics and field effect transistors.^[4]

The typical way to prepare cyclophanediene derivatives is through three-step procedures from their corresponding dithia[3.3]paracyclophane followed by benzyne Stevens rearrangement, oxidation and thermal elimination reaction.^[5] We have recently reported the synthesis of dioctyloxy diperfluorohexyl substituted [2.2]paracyclophane-1,9-diene from the corresponding dioctyloxy diperfluorohexyl dithia[3.3]paracyclophane.^[6] Unfortunately, benzyne Stevens rearrangement of

dithia[3.3]paracyclophane using traditional sources of benzyne generated *in situ* by the reaction of anthranilic acid and isoamyl nitrite at reflux condition in anhydrous 1,2-dichloroethane only gave the desired paracyclophanes in very poor yield.^[6,7] Relatively high yield of benzyne induced Stevens rearrangement of alkyl substituted dithia[3.3]paracyclophane can be achieved by the generation of benzyne through the reaction of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate with tetra-n-butylammonium fluoride (TBAF).^[8]

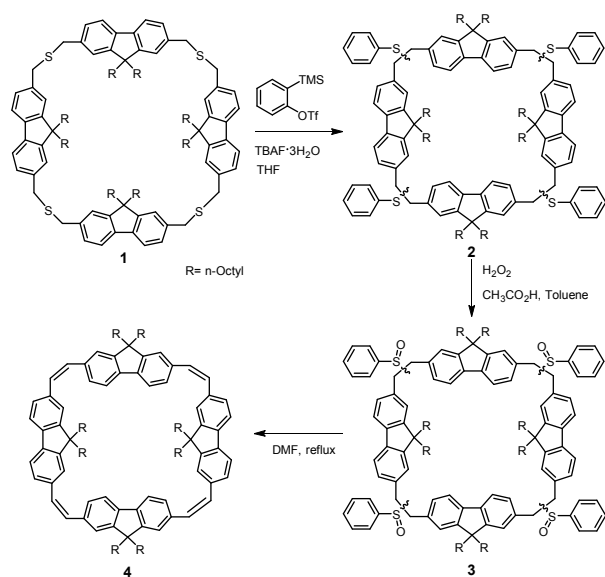
Considerable interest has developed recently in preparation of fluorenophane derivatives due to their remarkable fluorescent nature which may lead to potential applications in electronic, optoelectronic devices and fluorescence imaging.^[9] Although a few fluorenophanepolyenes such as unsubstituted *anti*-[2.2](2,7)-fluorenophanediene, [2.2.2](2,7)-fluorenophanetriene and their fluorenyl ions have been reported,^[10] no examples of alkyl substituted fluorenophanetetraene are available possibly due to multiple-step preparation and purification. In addition, ring opening of fluorenophanetetraene by photooxidation has not been reported. Herein we report, for the first time, the synthesis of octaoctyl substituted [2.2.2.2](2,7)-fluorenophanetetraene through three steps from octaoctyl substituted tetrathia[3.3.3.3]fluorenophanes followed by benzyne Stevens rearrangement, oxidation and pyrolysis reaction. In addition, all *trans*, linear fluorenevinylene with aldehyde end groups can be prepared by ring opening of fluorenophanetetraene by photooxidation. The spectroscopic and photophysical properties of this linear compound and fluorenophanetetraene were investigated and compared.

Results and discussion

Department of Materials Science and Engineering, National Taiwan University of Science and Technology, 43, Section 4, Keelung Road, Taipei, 10607, Taiwan.

Electronic Supplementary Information (ESI) available: the synthesis of starting materials for compound 1 and X-ray crystallographic data for CCDC 1556227 (compound 4). See DOI: 10.1039/x0xx00000x

The synthetic routes to octaoctyl substituted [2.2.2.2](2,7)-fluorenophanetetraene **4** are shown in **Scheme 1**. Octaoctyl-2,7-tetrathia[3.3.3.3]fluorenophane **1** was obtained by addition of a deoxygenated THF solution of an equimolar amount of 2,7-bis(bromomethyl)-9,9-dioctyl-9H-fluorene^[11] and (9,9-dioctyl-9H-fluorene-2,7-diyl)dimethanethiol^[11] to the deoxygenated ethanol with potassium hydroxide for at least 72 hours under a diluted solution. After complete addition, the reaction mixture was stirred for further 2 hours. The reaction mixture was extracted by dichloromethane and the solvent was evaporated under reduced pressure. The crude compound was purified by column chromatography using DCM: hexane (3:7) as the eluent. The major fraction was collected and recrystallized from toluene to give **1** as a white powder in a yield of 17 %. The yield is relatively low compared to other dithia[3,3]cyclophane made by this method possibly due to the formation of a large amount of undesired linear oligomers and polymers which did not come out from the silica gel column. It should be noted that there is no evidence for the formation of dithia[3,3]fluorenophane and trithia[3,3,3]fluorenophane after workup possibly due to the steric hindrance of octyl substituted fluorene units that leads to the difficulties of formation of dimers and trimers.



Scheme 1. The synthetic routes to octaoctyl substituted [2.2.2.2](2,7)-fluorenophanetetraene **4**.

The benzyne Stevens rearrangement of **1** can be prepared by the slow addition of tetrabutylammonium fluoride trihydrate (TBAF·3H₂O) to a THF solution of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate and **1**. The crude compound was purified by column chromatography using DCM: hexane (3:7) as the eluent. The benzyne Stevens rearrangement products contained a large number of stereoisomers and were not regioselective due to the migration of the phenyl sulfides to either carbon atoms of the thioether bond. The major fraction was then collected to give **2** in a

yield of 37 %. Compound **2** is very difficult to characterize by NMR spectroscopy due to the large numbers of signals overlapping. High resolution field desorption mass spectrometry gave a molecular ion of 2097.3925 for **2** (calculated for [M]⁺: 2097.3901). Compound **2** was then oxidized by H₂O₂ (35% w/w) in a mixture of acetic acid/toluene (1:3 volume ratio) at 0°C to give the desired compound **3**. Again, the ¹H NMR spectrum of **3** exhibited a complex range of signals and characterization was not possible. High resolution mass spectrometry gave a molecular ion with one sodium ion of 2184.3552 for **3** (calculated for [MNa]⁺: 2184.3601). The thermal elimination of **3** was in *N,N*-dimethylformamide at reflux under an argon stream for 18 hours. The crude compound was purified by column chromatography using hexane as the eluent to give the octaoctyl substituted [2.2.2.2](2,7)-fluorenophanetetraene **4** in a yield of 24 %.

The ¹H NMR spectrum of **1** in CDCl₃ is shown **Figure 1a**. A doublet at 7.79 ppm with *J* = 7.8 Hz integrating to eight hydrogens corresponds to the hydrogens of the fluorene rings which are *meta* position to the methylene groups bonded to sulfur atom. The doublet at 7.56 ppm (*J* = 7.8 Hz) integrating to eight hydrogens is associated with *ortho* position of the hydrogens of the fluorene rings to the methylene groups linked to sulfur atom. The singlet at 7.21 ppm corresponding to eight hydrogens is assigned to the *ortho* position of the aromatic hydrogens to quaternary carbons attached to alkyl chains. The singlet at 3.58 ppm corresponding to sixteen hydrogens is corresponding to the thioether hydrogens. The other peaks below 2.50 ppm are corresponding to the hydrogens of the alkyl chains.

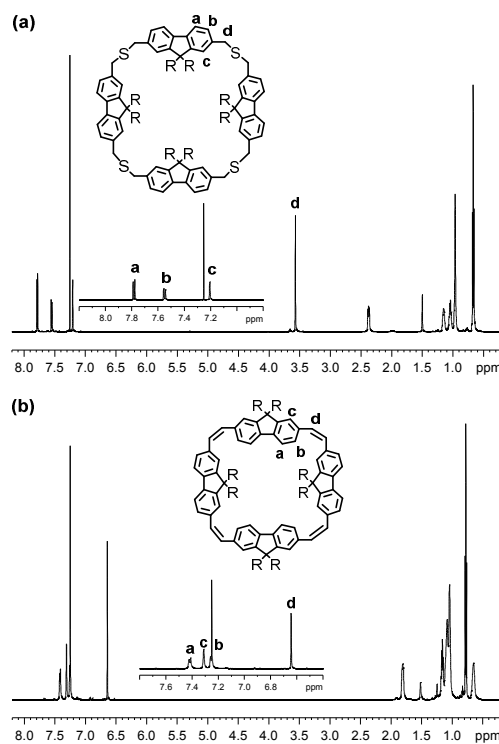


Figure 1. The ^1H NMR spectra (CDCl_3) of (a) octaoctyl substituted 2,7-tetrathia[3.3.3.3]fluorenophane **1** and (b) octaoctyl substituted [2.2.2.2](2,7)-fluorenophanetetraene **4**. The signals corresponded to the aromatic and vinylic hydrogens are shown in the insets.

The ^1H NMR spectrum of **4** in CDCl_3 is shown in **Figure 1b**. There is a doublet at 7.80 ppm with $J = 7.8$ Hz (eight hydrogens) assigned to the *meta* position of the aromatic hydrogens to the methine groups. The singlet at 7.32 ppm integrating to eight hydrogens corresponds to the *ortho* position of the aromatic hydrogens to quaternary carbons attached to alkyl chains. The doublet at 7.26 ppm ($J = 7.8$ Hz) integrating to eight hydrogens can be assigned to *ortho* position of the aromatic hydrogens to the methine groups. The singlet at 6.65 ppm integrating to eight hydrogens is associated to the *cis*-vinylic hydrogens. The other peaks below 2.00 ppm are corresponding to the hydrogens of the alkyl chains. This can also be determined by high resolution mass spectrometry giving a molecular ion of 1657.3149 (calculated for $[\text{M}]^+$: 1657.3141).

A single crystal of **4** can be obtained by the vapor diffusion techniques at the room temperature using 1,4-dioxane and ethanol as a solvent system. The solid-state X-ray crystallography of **4** (**Figure 2**) clearly shows that the fluorene units linked by *cis* vinylenes. There are two orientations of alkyl chains being inward and outward of the rings. The average bond length of vinylenes for compound **4** is 1.33 Å which is in agreement with those of a standard *cis*-vinylenes bond (1.32 Å).^[12] The average C(aryl)-C(methine) bond length is 1.48 Å. The torsion angle of the individual vinylic linkages is 9.4°, 5.2°, 4.0° and 0.6°. The distance between adjacent centroids of fluorenes is 8.33 Å, 8.40 Å, 7.57 Å and 7.62 Å which is much larger than that of unsubstituted fluorenophanediene and fluorenophanetriene.^[10] This suggests that there is little transannular π - π overlap. It should be noted that some of the atoms at the end of alkyl chains are disordered because it is very difficult to obtain the high quality of the crystal in such a molecule containing a large number of atoms.

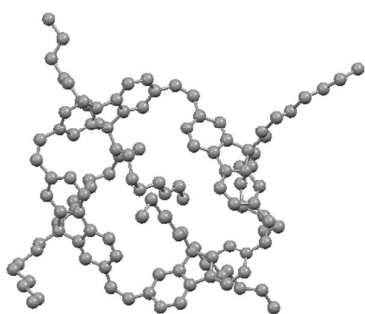


Figure 2. Solid-state structure of **4**. Hydrogen atoms are omitted for clarity.

A photooxidation reaction of **4** can be carried out in dilute hexane solution (6×10^{-7} M) under an oxygen atmosphere using a 6

watt TLC UV lamp at a wavelength of 365 nm. The absorption and photoluminescence spectra of **4** under the UV light irradiation for a period of time are shown in **Figure 3**. The absorbance of **4** at 345 nm gradually decreases with increases the absorbance at 412 nm as irradiation time goes on. When **4** was exposed to UV light for 120 minutes, the original peak (345 nm) has nearly disappeared and the additional absorption peak at 412 nm has reached to highest absorbance. In addition, the emission intensity increases with clearly three emission peaks at 449, 478 and 513 nm compared to initial state of **4**. This suggests that **4** was underwent photooxidation reaction which may lead to open the ring of **4**. In order to prove that the UV light irradiation and the presence of oxygen are essential for ring opening of **4**, compound **4** was then carried out in dilute hexane solution (6×10^{-7} M) either exclusive under the UV light irradiation or in the presence of oxygen. The results of both cases reveal that there is little change in the absorption spectra of **4** for a period of time (see electronic supplementary information).

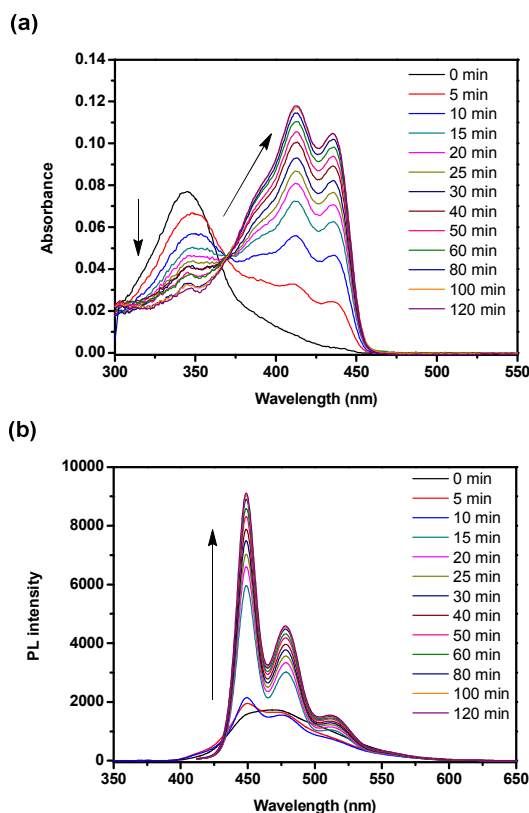


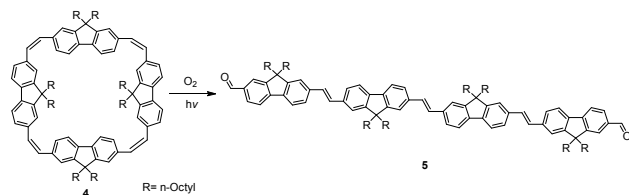
Figure 3. (a) UV-vis absorption and (b) PL spectra (right) of **4** in dilute hexane solution under the UV light irradiation for a period of time. Arrows in the figures show the direction of change in the spectra with increasing the irradiation time.

In order to obtain a decent amount of compound for the structure identification after a photooxidation reaction, a more concentrated hexane solution of **4** was irradiated under UV light. An

ARTICLE

Journal Name

extended period of time is needed for completion of the photooxidation reaction due to the rate of photooxidation reaction was slower in more concentrated solution.^[13] The crude compound was then purified by column chromatography using hexane/DCM (7:3) as the eluent to give **5** in a yield of 78 % (Scheme 2).



Scheme 2. Ring opening reaction of octaoctyl substituted [2.2.2.2](2,7)-fluorenophanetetraene **4** by photooxidation to give **5**.

The ¹H NMR spectrum of **5** (Figure 4) shows a singlet at 10.07 ppm corresponding to the hydrogens of aldehyde groups (a). The singlet at 7.88 ppm can be assigned to the *ortho* position of the aromatic hydrogens (k) to the aldehyde groups and the quaternary carbons attached to alkyl chains. Two doublets at 7.86 and 7.83 ppm associated to each other with *J* = 7.8 Hz corresponds to *meta* and *ortho* positions of the aromatic hydrogens (j and i) to the aldehyde groups. The two doublets at 7.78 and 7.59 ppm coupling to each other with *J* = 7.8 Hz are assigned to *meta* and *ortho* positions of the aromatic hydrogens (h and d) to the methine groups. A doublet at 7.70 ppm with *J* = 7.8 Hz are associated with the aromatic hydrogens (g). The multiplet at around 7.56 can be assigned to the aromatic hydrogens c and f. A singlet at 7.53 ppm can be assigned to the aromatic hydrogens (e). The multiplet at around 7.30 ppm can be assigned to the *trans*-vinylic hydrogens (b). The other peaks below 2.20 ppm are associated with alkyl chain hydrogens. No peaks can be detected at 6.65 ppm and the multiplet can be observed at around 7.30 ppm which indicates that all *cis*-vinylens of **4** transform to all *trans* conformation after photooxidation. High resolution mass spectrometry gave a molecular ion of 1689.3067 (calculated for [M]⁺: 1689.3039).

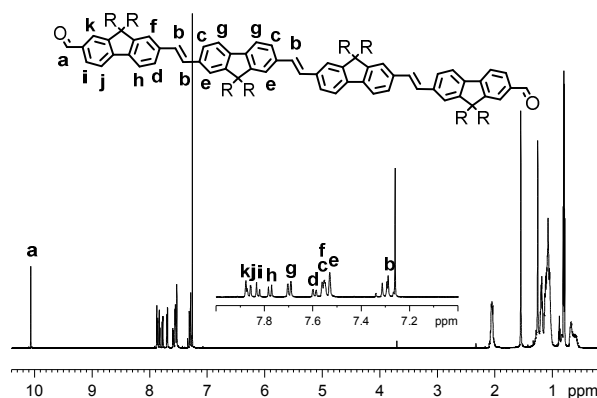


Figure 4. ¹H NMR spectrum (CDCl₃) of **5**. The signals corresponded to the aromatic and vinylic hydrogens are shown in the insets..

The absorption spectra and emission spectra of **4** and **5** were recorded in dilute hexane solution (Figure 5). The absorption maximum of **5** is at 412 nm which reveals large red-shifted by 67 nm compared to **4** (345 nm) possibly due to the better planarity and longer conjugation lengths. The small Stokes shift (37nm) and three notable emission peaks can be observed at 449, 478 and 513 nm for **5** possibly due to the formation of more rigid structure than cyclic compound **4**.^[14] The photoluminescence quantum yield of **5** is 0.73 which is higher than **4** (0.43).

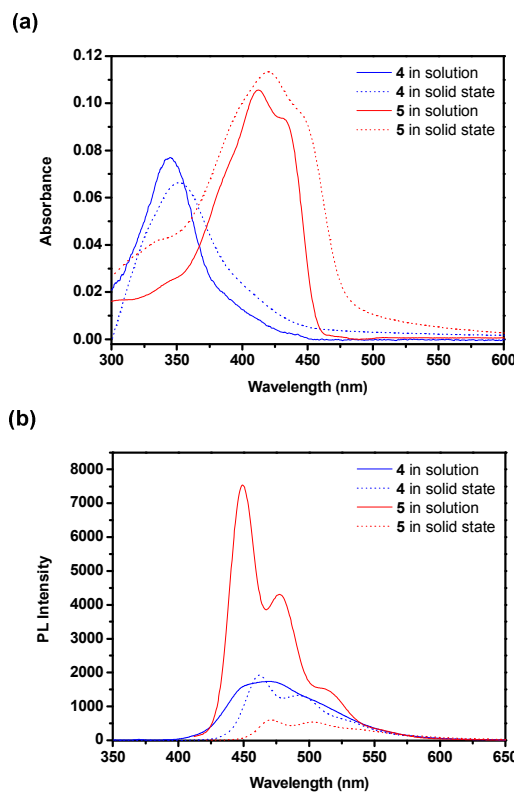


Figure 5. The (a) UV-vis and (b) PL spectra of **4** and **5**.

Thin films of **4** and **5** were prepared by spin coating a hexane solution (1 mg/mL) onto glass substrates at room temperature. The solid state absorption maximum of **4** is at 352 nm which is red-shifted by 7 nm from those carried out in solution. However, the solid state emission maximum of **4** is at 462 nm which is blue-shifted by 6 nm from those carried out in solution. The plausible explanation is that the electronic transition is different between solution and solid state. The solid state absorption maximum of **5** is at 421 nm which is red-shifted by 9 nm from those carried out in solution and the solid state emission maximum of **5** is at 471 nm which is red-shifted by 22 nm from those carried out in solution. This bathochromic shift is attributed to intermolecular interactions as in the solid state. The optical bandgap of **5** calculated from the onset of the absorption is 2.56 eV which is smaller than that of **4** (2.76 eV). Interestingly, compound **4** in solid state exhibited higher

fluorescence intensity than that of **5** indicating that there is little intermolecular interaction.

Experimental

Materials and instrumentation

All reagents were from commercial sources and were used without further purification. Solvents used for spectroscopic measurements were spectrograde. Most of the reactions were monitored by thin-layer chromatography carried out on silica gel plates. Preparative separations were performed by column chromatography on silica gel grade 60 (0.040 – 0.063 mm) from Merck. The starting materials, 2,7-bis(bromomethyl)-9,9-dioctyl-9H-fluorene and (9,9-dioctyl-9H-fluorene-2,7-diyl)dimethanethiol, were synthesized by previously established synthetic methods (more details see electronic supplementary information).^[11] Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker ultrashield spectrometer operating at 600 MHz for ¹H nuclei and 150 MHz for ¹³C nuclei. Chemical shifts are reported in ppm. All coupling constants are reported in hertz (Hz). The abbreviations are used to indicate multiplicity: s = singlet, d = doublet, dd = doublet of doublets, t = triplet and m = multiplet. UV-vis absorption and photoluminescence spectra were recorded on the Jasco (V-670) UV-Vis-NIR spectrophotometer and on the Jasco (FP-8500) fluorescence spectrophotometer, respectively. X-ray crystallographic data for single crystals were determined using a Bruker Kappa APEX II diffractometer equipped with an Oxford Cryosystems 700 series cryostream cooler using graphite monochromated Mo-K_α radiation. Electron ionization (EI) and field desorption (FD) mass spectra were recorded on a JEOL (AccuTOF GCX) of high resolution gas chromatograph mass spectrometer. Elemental analyses were performed on a Heraeus varioIII-NCSH elemental analyzer.

Synthesis

Synthesis of octaoctyl substituted 2,7-tetrathia[3.3.3.3]fluorenophane **1**: A deoxygenated mixture of 2,7-bis(bromomethyl)-9,9-dioctyl-9H-fluorene (5.74 g, 9.96 mmol) and (9,9-dioctyl-9H-fluorene-2,7-diyl)dimethanethiol (4.80 g, 9.96 mmol) in THF (360 mL) was added dropwise to a deoxygenated solution of KOH (1.66 g, 29.59 mmol) in 95% ethanol (540 mL) under an argon atmosphere for a period of 72 hours. After completely addition, the reaction mixture was stirred at room temperature for additional 2 hours. The most of the solvent was then removed and the residue was extracted with HCl and DCM several times. The organic layers were combined, washed with water, dried with anhydrous MgSO₄, filtered and evaporated. The residue was then purified by column chromatography using DCM: hexane (3:7) as the eluent. The major fraction was collected and recrystallized from toluene to give **1** in a yield of 17 % (2.93 g). ¹H NMR (600 MHz, CDCl₃): δ 7.79 (d, J = 7.8 Hz, 8H, ArH), 7.56 (d, J = 7.8 Hz, 8H, ArH), 7.21 (s, 8H, ArH), 3.58 (s, 16H, ArCH₂S-), 2.38 (m, 16H), 1.16 (m, 16H), 1.05 (m, 16H), 0.97 (m, 48H), 0.67 (m, 40H, -CH₃- and -CCH₂CH₂-). ¹³C NMR (150 MHz, CDCl₃): δ 149.95, 140.50, 137.45, 128.36, 124.07, 120.92, 55.37, 41.77, 34.11, 31.99, 30.87, 30.16, 29.42, 24.46, 22.67, 14.07. HR-MS (FD, [M]⁺): calculated for [C₁₂₄H₁₇₆S₄]⁺: m/z 1793.2650, found m/z 1793.2623. Elemental

analysis: found: C, 83.59; H, 9.79; S, 6.73 %; calculated for C₁₂₄H₁₇₆S₄: C, 82.97; H, 9.88; S, 7.14 %.

Synthesis of benzyne Stevens rearrangement products **2**: A suspension of octaoctyl substituted 2,7-tetrathia[3.3.3.3]fluorenophane (2.1 g, 1.17 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1.70 g, 5.68 mmol) was dissolved in anhydrous THF (45 mL) at room temperature under an argon atmosphere. Tetrabutylammonium fluoride trihydrate (2.14 g, 6.8 mmol) was dissolved in anhydrous THF (13 mL) and added dropwise to the former solution over 30 minutes. The solution was stirred for additional an hour and the solvent was removed to give to a pale yellow oil. The residue was purified by column chromatography using DCM/hexane (3:7) as the eluent. Major fraction was collected and gave **2** in a yield of 37 % (0.91 g). HR-MS (FD, [M]⁺): calculated for [C₁₄₈H₁₉₂S₄]⁺: m/z 2097.3901, found m/z 2097.3925.

Synthesis of tetrasulfoxide compound **3**: H₂O₂ (0.15 mL, 35 wt %) was added dropwise to a solution of **2** (0.93 g, 0.44 mmol) in toluene (21 mL) and acetic acid (6.8 mL) at 0°C. After finishing the addition, the solution was allowed to warm to room temperature and stirred for additional 12 hours. The solution was extracted with water and DCM and the combined organic layers were washed with water, dry with anhydrous MgSO₄, filtered and evaporated. The crude compound was then purified by column chromatography using DCM as an eluent. The major fraction was collected and gave **3** in a yield of 90 % (0.86 g). HR-MS (TOF ES, [MNa]⁺): calculated for [C₁₄₈H₁₉₂O₄S₄Na]⁺: m/z 2184.3601, found m/z 2184.3552.

Synthesis of octaoctyl substituted [2.2.2.2](2,7)-fluorenophanetetraene **4**: Compound **3** (0.98 g, 0.45 mmol) was dissolved in N,N-dimethylformamide (70 mL) and stirred at reflux for 20 hours under an argon stream. The reaction was then cooled to room temperature and extracted with dilute HCl and DCM, dried with anhydrous MgSO₄, filtered and evaporated to give yellow oil. The crude compound was purified by column chromatography using hexane as the eluent to give **4** in a yield of 24 % (0.18 g). ¹H NMR (600 MHz, CDCl₃): δ 7.43 (d, J = 7.8 Hz, 8H, ArH), 7.32 (s, 8H, ArH), 7.26 (d, J = 7.8 Hz, 8H, ArH), 6.65 (s, 8H, ArCH=CH-), 1.82 (m, 16H), 1.17 (m, 16H), 1.09 (m, 16H), 1.05 (m, 48H), 0.79 (t, J = 7.3 Hz, 24H, -CH₃), 0.66 (m, 16H, -CCH₂CH₂-). ¹³C NMR (150 MHz, CDCl₃): δ 151.14, 140.17, 136.35, 130.44, 127.60, 123.68, 119.33, 55.02, 40.34, 32.02, 30.27, 29.53, 29.47, 23.97, 22.77, 14.21. HR-MS (FD, [M]⁺): calculated for [C₁₂₄H₁₆₈]⁺: m/z 1657.3141, found m/z 1657.3149. Elemental analysis: found: C, 89.64; H, 10.15 %; calculated for C₁₂₄H₁₆₈: C, 89.79; H, 10.21 %.

Synthesis of compound **5**: A solution of octaoctyl substituted [2.2.2.2](2,7)-fluorenophanetetraene **4** (0.025 g, 0.015 mmol) in hexane (300 mL) was exposed under UV light irradiation (TLC-UV lamp, 365 nm, 6 watt) over 24 hours. The crude compound was purified by column chromatography using hexane/DCM (7:3) as the eluent and give **5** in a yield of 78 % (0.02 g). ¹H NMR (600 MHz, CDCl₃): δ 10.07 (s, 2H, -CHO), 7.88 (s, 2H, ArH), 7.86 (d, J = 7.8 Hz, 2H, ArH), 7.83 (d, J = 7.8 Hz, 2H, ArH), 7.78 (d, J = 7.8 Hz, 2H, ArH), 7.70 (d, J = 7.8 Hz, 4H, ArH), 7.59 (d, J = 7.8 Hz, 2H, ArH), 7.56 (m, 6H, ArH), 7.53 (s, 4H, ArH), 7.30 (m, 6H, ArCH=CH-), 2.05 (m, 16H),

ARTICLE

Journal Name

1.35-1.00 (m, 80H), 0.80 (m, 24H), 0.63 (m, 16H). HR-MS (FD, [M]⁺): calculated for [C₁₂₄H₁₆₈O₂]⁺: m/z 1689.3039, found m/z 1689.3067.

Conclusions

Octaoctyl substituted fluorenophanetetraene was successfully prepared from octaoctyl substituted tetrathia[3.3.3.3]fluorenophanes in three steps through benzyne Stevens rearrangement, oxidation and thermal elimination reaction. The octaoctyl substituted fluorenophanetetraene was fully characterized by nuclear magnetic resonance spectroscopy, high resolution mass spectrometry and X-ray crystallography. The photooxidation reaction of the fluorenophanetetraene was carried out in dilute solution under UV light irradiation to give all *trans* linear fluorenevinylene with aldehyde end groups. The optical properties of fluorenophanetetraene and its linear compound generated by photooxidation have been investigated and compared. These cyclic conjugated molecules will be of tremendous interest to those chemists and physicists interested in fluorescent devices, organic transistors and organic photovoltaics in general. Thermal and photoinduced ring-opening metathesis polymerization of fluorenophanetetraene is currently under investigation.

Acknowledgements

The authors thank the financial support from the National Taiwan University of Science and Technology and the Ministry of Science and Technology.

Notes and references

- a) C.-L. Wang, Y.-C. Chang, C.-M. Lan, C.-F. Lo, E. W.-G. Diao, C.-Y. Lin, *Energy Environ. Sci.* 2011, **4**, 1788–1795; b) S. Yamago, E. Kayahara, T. Iwamoto, *Chem. Rec.* 2014, **14**, 84–100; c) X.-F. Wang, H. Tamiak, *Energy Environ. Sci.* 2011, **4**, 1788–1795; d) K. Mouri, S. Saito, S. Yamaguchi, *Angew. Chem. Int. Ed.* 2012, **51**, 5971–5975; e) N. Aratani, D. Kim, A. Osuka, *Acc. Chem. Res.* 2009, **42**, 1922–1934; f) Y. Song, C. Di, X. Yang, S. Li, W. Xu, Y. Liu, L. Yang, Z. Shuai, D. Zhang, D. Zhu, *J. Am. Chem. Soc.* 2006, **128**, 15940–15941.
- a) Y.-H. Lai, P. Chen, *J. Org. Chem.* 1989, **54**, 4586–4590; b) Y.-H. Lai, Z.-L. Zhou, *J. Chem. Soc., Perkin Trans. 2* 1994, 2361–2365; c) S. Muratsugu, S. Kume, H. Nishihara, *J. Am. Chem. Soc.* 2008, **130**, 7204–7205; d) K. Ayub, R. H. Mitchell, *J. Org. Chem.* 2014, **79**, 664–678; e) C.-W. Chu, M. Horie, *Asian J. Org. Chem.* 2013, **2**, 838–842; f) K. C. Dewhurst, D. J. Cram, *J. Am. Chem. Soc.* 1958, **80**, 3115–3125. g) H. Hopf, *Angew. Chem. Int. Ed.* 2008, **47**, 9808–9812. h) G. J. Bodwell, T. Satou, *Angew. Chem. Int. Ed.* 2002, **41**, 4003–4006. i) K. Okamoto, C. K. Luscombe, *Polym. Chem.* 2011, **2**, 2424–2434.
- a) C.-Y. Yu, M. L. Turner, *Angew. Chem. Int. Ed.* 2006, **45**, 7797–7800; b) A. M. Spring, C.-Y. Yu, M. Horie, M. L. Turner, *Chem. Commun.* 2009, 2676–2678; c) C.-Y. Yu, J. W. Kingsley, D. G. Lidzey, M. L. Turner, *Macromol. Rapid Commun.* 2009, **30**, 1889–1892; d) C.-Y. Yu, M. Horie, A. M. Spring, K. Tremel, M. L. Turner, *Macromolecules* 2010, **43**, 222–232; e) B. J. Lidster, J. M. Behrendt, M. L. Turner, *Chem. Commun.* 2014, **50**, 11867–11870; f) D. Mäker, C. Maier, K. Brödner, U. H. F. Bunz, *ACS Macro Lett.* 2014, **3**, 415–418. g) C.-Y. Yu, S.-H. Yu, S.-H. Wen, C.-C. Wang, *Tetrahedron Lett.* 2017, **58**, 3854–3858.
- a) A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem. Rev.* 2009, **109**, 897–1091; b) B. Wang, M. R. Wasielewski, *J. Am. Chem. Soc.* 1997, **119**, 12–21; c) L. -L. Chua, J. Zaumseil, J. -F. Chang, E. C.-W. Ou, P. K.-H. Ho, H. Sirringhaus, R. H. Friend, *Nature* 2005, **434**, 194–199; d) T. Kietzke, D. A. M. Egbe, H.-H. Hörhold, D. Neher, *Macromolecules* 2006, **39**, 4018–4022.
- a) T. Otsubo, V. Boekelheide, *Tetrahedron Lett.* 1975, **16**, 3881–3884; b) C. A. Kingsbury, D. J. Cram, *J. Am. Chem. Soc.* 1960, **82**, 1810–1819; c) B. M. Trost, A. J. Bridges, *J. Org. Chem.* 1975, **40**, 2014–2016.
- C.-Y. Yu, C.-H. Sie, C.-Y. Yang, *New J. Chem.* 2014, **38**, 5003–5008.
- C.-Y. Yu, M. Helliwell, J. Raftery, M. L. Turner, *Chem. Eur. J.* 2011, **17**, 6991–6997.
- a) A. Cobas, E. Guitián, L. Castedo, *J. Org. Chem.* 1997, **62**, 4896–4897; b) B. J. Lidster, D. R. Kumar, A. M. Spring, C.-Y. Yu, M. Helliwell, J. Raftery, M. L. Turner, *Org. Biomol. Chem.* 2016, **14**, 6079–6087.
- a) T. Tsuge, R. Nada, T. Moriguchi, K. Sakata, *J. Org. Chem.* 2001, **66**, 9023–9025; b) P. Rajakumar, R. Kanagalatha, *Tetrahedron Lett.* 2007, **48**, 2761–2764; c) M. A. Majewski, T. Lis, J. Cybińska and M. Stępień, *Chem. Commun.* 2015, **51**, 15094–15097.
- K. Matsumoto, H. Minami, T. Kawase, Masaji Oda, *Org. Biomol. Chem.* 2004, **2**, 2323–2326.
- a) P. Taranekar, M. Abdulbaki, R. Krishnamoorti, S. Phanichphant, P. Waenkaew, D. Patton, T. Fulghum, R. Advincula, *Macromolecules* 2006, **39**, 3848–3854; b) K.Y. Kay, I. C. Oh, *Tetrahedron Lett.* 1999, **40**, 1709–1712.
- F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* 1987, S1–S19.
- a) N. Shimizu, P. D. Bartlett, *J. Am. Chem. Soc.* 1976, **98**, 4193–4200; b) P. D. Bartlett, M. E. Landis, *J. Am. Chem. Soc.* 1977, **99**, 3033–3037.
- C. Wetzal, E. Brier, A. Vogt, A. Mishra, E. Mena-Osteritz, P. Bäuerle, *Angew. Chem. Int. Ed.* 2015, **54**, 12334–12338.

Table of Contents

Octa-octyl substituted fluorenophanetetrane has been synthesized and the photooxidation of fluorenophanetetrane gives all *trans* linear fluorenevinylene with aldehyde end groups.

