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Stacked 1,3,5-tris[(2,5-dimethylphenyl)ethynyl]benzenes: dimer and conjugated microporous polymer

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ABSTRACT

A new [2.2]paracyclophane compound consisting of two 1,3,5-tris[(2,5-dimethylphenyl)ethynyl]benzenes stacked in proximity to each other. The compound exhibited a unique absorption band (cyclophane band) and an emission from the phane state, both of which were derived from the π–π stacking of the poorly extended conjugation systems of 1,3,5-tris[(2,5-dimethylphenyl)ethynyl]benzene. In addition, a conjugated microporous polymer (CMP) that comprises pseudo-*para*-substituted [2.2]paracyclophane was prepared. The obtained CMP is regarded as a polymer, in which 1,3,5-tris[(2,5-dimethylphenyl)ethynyl]benzenes are infinitely stacked to form a network structure. The CMP exhibited a type I nitrogen gas sorption profile and an H4-like hysteresis loop, and possessed the slit-like mesopores with a BET surface area of 501 m^2 g^{-1}.

Introduction

[2.2]Paracyclophane, in which two benzene rings are connected with two ethylenes at the *para*-positions, has attracted the attention of researchers owing to its structure, reactivity, and physical properties. The distance between the bridge carbon atoms is approximately 2.8 Å, and that between the centers of the two benzene rings is approximately 3.1 Å; thus, a π–π interaction exists in [2.2]paracyclophane because this distance is shorter than the sum of the van der Waals radii of an sp^2 carbon (3.40 Å). Since the first report on the practical synthesis of [2.2]paracyclophane,[1] a variety of cyclophane derivatives have been prepared, and their unique structural and electronic properties arising from the longitudinal π–π interaction between the co-facial aromatic rings have been investigated in detail.[2]

By the introduction of two π-electron systems into a [2.2]paracyclophane skeleton, two chromophores are constrained to be stacked in proximity to each other. The electronic structure of such a [2.2]paracyclophane compound depends on its π-conjugation length, orientation, and the overlapping position of the stacked chromophores.[3] For example, the photoluminescence spectrum of stilbene dimer **1** is broad and featureless with a low fluorescence quantum efficiency (Φ_{PL}), while that of compound **2** shows a vibrational structure with a high Φ_{PL}. The emission of **1** is derived from the phane state, that is, excimer-like emission, while that of **2** is derived from the monomer (chromophore) state (Fig. 1).

Our previous work showed that the incorporation of [2.2]paracyclophane into a conjugated polymer backbone results in the formation of a π-stacked structure in a single polymer chain.[4] The polymers containing [2.2]paracyclophane as a repeating unit have extended conjugation lengths via the stacked π-electron systems, and despite the stacked structures in the polymer main chain, they

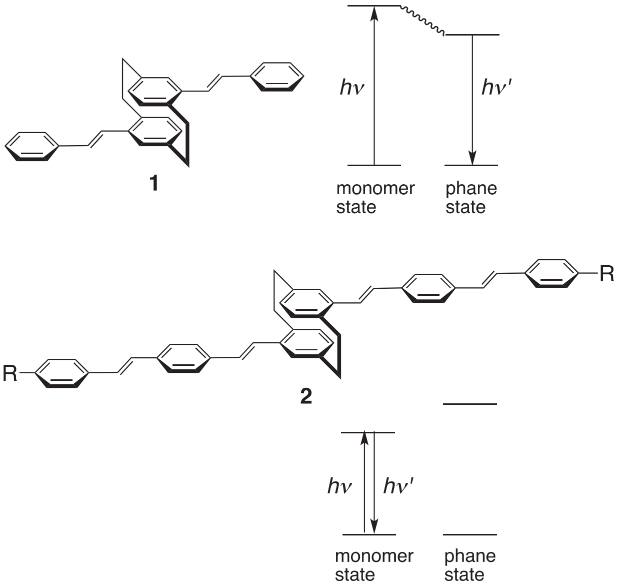

Figure 1. Emission mechanism of cyclophane compounds.

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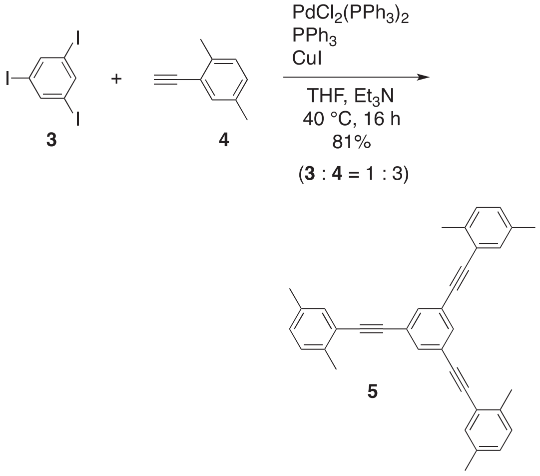
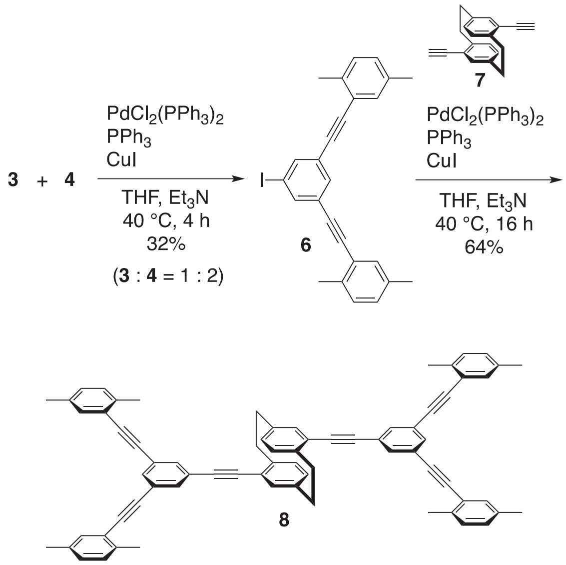


Scheme 1. Synthesis of compound **5**.



Scheme 2. Synthesis of compound **8**.

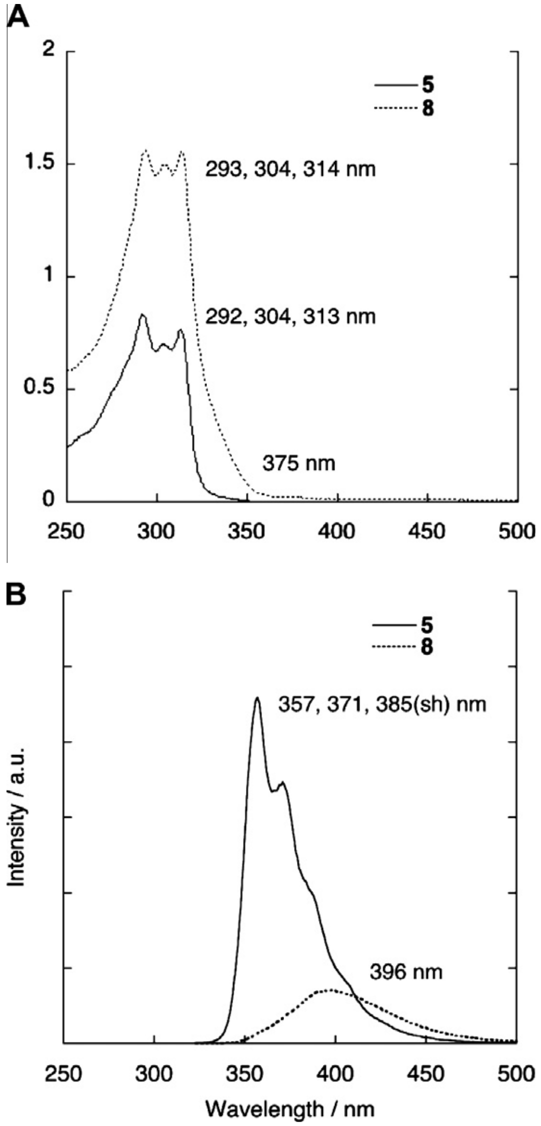


Figure 2. (A) UV–vis absorption spectra of compounds **5** and **8** in CH_2Cl_2 (1.0×10^{-5} M). (B) Photoluminescence spectra of **5** and **8** in CH_2Cl_2 (1.0×10^{-5} M) excited at 313 nm.

emit high Φ_{PL} due to the emission from the monomer (chromophore) state. Thus, [2.2]paracyclophane can be used as a scaffolding on which various π-electron systems can be stacked, leading to a better understanding of their through-space interactions. In this Letter, we report on the synthesis, characterization, and optical properties of a new [2.2]paracyclophane compound comprising of two 1,3,5-tris[(2,5-dimethylphenyl)ethynyl]benzenes stacked in proximity to each other. In addition, we prepared a conjugated microporous polymer (CMP) that consists of pseudo-*para*-substituted [2.2]paracyclophane. The obtained CMP is regarded as a polymer, in which 1,3,5-tris[(2,5-dimethylphenyl)ethynyl]benzenes are infinitely stacked to form a network structure; the synthesis and characterization are also described.

Results and discussion

The synthesis of 1,3,5-tris[(2,5-dimethylphenyl)ethynyl]benzene **5** was carried out as the model compound of the monolayer unit. As shown in Scheme 1, Sonogashira–Hagihara coupling[5] of 1,3,5-triiodobenzene **3** with 3 equiv of ethynylxylene **4** proceeded smoothly to obtain **5** in 81% isolated yield. When 2 equiv of **4** was reacted, 1-iodo-3,5-bis[(2,5-dimethylphenyl)ethynyl]benzene **6** was mainly obtained in 32% isolated yield (Scheme 2). 1,3-Diiodo-5-[(2,5-dimethylphenyl)ethynyl]benzene and **5** were also obtained as by-products, which were readily removed by standard SiO_2 column chromatography (Supplementary data). 1,3,5-Tris[(2,5-dimethylphenyl)ethynyl]benzene-stacked compound **8** was prepared using pseudo-*para*-diethynyl[2.2]paracyclophane **7** as a building block.[6,7] Thus, the reaction of **6** with **7** in the presence of a catalytic amount of $PdCl_2(PPh_3)_2/PPh_3/CuI$ afforded **8** in 64% isolated yield (Scheme 2). Owing to the [2.2]paracyclophane framework, two 1,3,5-tris[(2,5-dimethylphenyl)ethynyl]benzenes are constrained to partially overlap one another and to be stacked in proximity by two ethylene chains.

The structures of **5** and **8** were confirmed by ^1H and ^{13}C NMR spectroscopy, and the spectra are shown in the Supplementary data. In the ^1H NMR spectrum of **5** (Fig. S1), the signals of xylene protons appeared at 7–7.5 ppm, while the signals of the aromatic protons of **8** were observed at around 6.5 ppm (Fig. S7). These signals in the higher magnetic field are assigned to the aromatic protons in the [2.2]paracyclophane moiety produced because of the ring current effect.

The UV–vis absorption spectra of **5** and **8** in CH_2Cl_2 (1.0×10^{-5} M) are shown in Figure 2A. The spectrum of **5** exhibited vibrational structures with peak top wavelengths of 292, 304, and 313 nm. This spectrum was similar to that of tris(phenylethynyl)benzene, and it red-shifted by approximately 10 nm.[8] It is reported that such a red-shift was observed with the donor substitution; the absorption spectra of tris(phenylethynyl)benzenes are red-shifted by substitution of the donor methoxy group.[9] The shape of the absorption spectrum of **8** was identical to that of **5** (Fig. 2A), and the molar extinction coefficient (ε) of **8** was almost twice that of **5** due to the π-stacked dimer. In the spectrum of **8**, however, a typical cyclophane band was observed at around 375 nm as a broad peak with low absorbance.

The photoluminescence (PL) spectra of **5** and **8** in CH_2Cl_2 (1.0×10^{-5} M) were obtained with an excitation wavelength of 313 nm (Fig. 2B). We confirmed that this concentration was sufficiently diluted (Fig. S9 in Supplenentary data) without intermolecular interactions. Compound **5** exhibited a sharp PL spectrum with a vibrational structure, which was also similar to the spectrum of tris(phenylethynyl)benzene. The absolute PL quantum efficiency (Φ_{PL}) of **5** was calculated to be 0.24. The π-stack structure caused a red-shift of the PL spectrum and a decrease in Φ_{PL}; thus, the PL spectrum of **8** was broad and featureless, and the $\lambda_{PL,max}$ of **8** was observed at around 396 nm with a Φ_{PL} of 0.16. These results indicate that emission by **8** occurs from the phane state rather than the monomer state due to the poorly extended conjugation system of the stacked π-electron system, that is, the π-electron system of **5**. The PL spectra of **5** and **8** in the solid state are shown in Figures S10A and S11A, respectively. Due to the intermolecular interaction, both peaks were red-shifted in comparison with those of the solutions. On the other hand, **5** and **8** were well-dispersed in the polystyrene matrix (cast film including 1.0×10^{-2} wt % of **5** and **8**), and their spectra were similar to those in solutions (Figs. S10B and S11B, respectively).

By stacking 1,3,5-tris[(2,5-dimethylphenyl)ethynyl]benzenes repeatedly, a network polymer can be prepared. Recently, network polymers consisting of rigid-rod conjugated frameworks possessing micropores, which are called conjugated microporous polymers (CMPs), have been extensively studied.[10,11] As shown in Scheme 3, the treatment of **3** with **7** in the presence of a catalytic amount of $Pd(PPh_3)_4$ and CuI at 80 °C for 72 h yielded a pale yellow precipitate. The reaction was quenched with 1.0 N aqueous HCl, and the obtained precipitate was washed with $CHCl_3$ and MeOH (each for 24 h) using a Soxhlet extractor. Then, after it was heated at 70 °C under vacuum for 24 h, CMP **P1** was obtained in 114% isolated yield. Generally, the isolated yield of a CMP prepared by palladium-catalyzed coupling is over 100% owing to the unreacted halogens. In the case of **P1**, it was found to contain 3.40 wt % of iodine according to the elemental analysis.

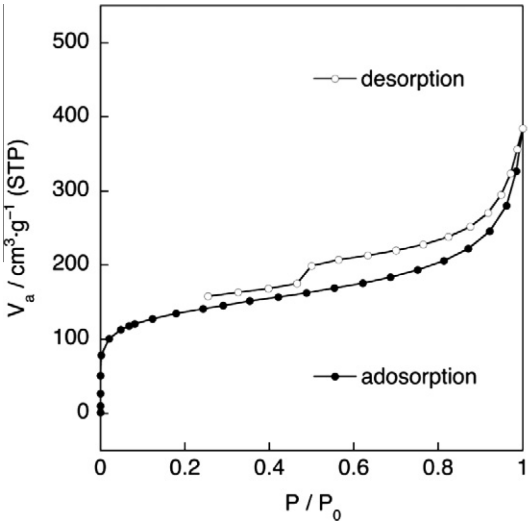
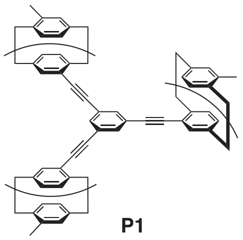
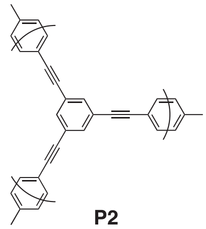


Figure 3. N_2 adsorption–desorption isotherm of CMP **P1** at 77 K.

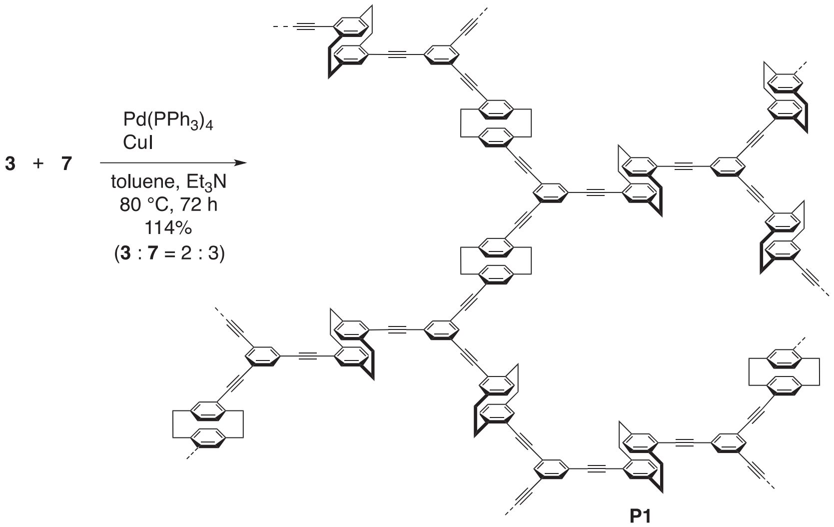


P1



P2

The structure of **P1** was confirmed by solid-state CP MAS ^{13}C NMR spectrum and FTIR spectrum, as shown in Figures S12 and S13, respectively (Supplementary data). In addition, the characterization of **P1** was carried out by scanning electron microscopy (SEM, Fig. S16), X-ray diffraction analysis (XRD, Fig. S18), and nitrogen sorption analysis. Figure 3 shows the nitrogen adsorption–desorption isotherm of **P1** measured at 77 K. The isotherm was categorized as the type I nitrogen gas sorption profile



P1

Scheme 3. Synthesis of CMP **P1**.

according to the IUPAC classification,[12] and it was associated with an H4-like hysteresis loop, indicating the existence of narrow slit-like pores. Thus, the incorporation of the step structure of the [2.2]paracyclophane moiety formed the slit-like mesopores, and the Brunauer–Emmett–Teller (BET) surface area (S_{BET}) was estimated to be 501 $m^2\,g^{-1}$. On the other hand, it has been reported that the CMP **P2** with phenylene instead of [2.2]paracyclophane possesses a larger surface area of 834 $m^2\,g^{-1}$.[11a,c,13] The two-dimensional network in **P1** probably arises from the step and stacked structure of the [2.2]paracyclophane unit in addition to the three-dimensional network, while the three-dimensional network structure is effectively created in **P2** by the bending of the struts, which leads to a larger surface area. The differences in these structures reflect their morphologies.[11a] The SEM image of **P1** reveals the aggregates of masses and plates (Fig. S16), while that of **P2** shows the aggregates of spherical particles (Fig. S17).[14]

Conclusion

In conclusion, we have synthesized a new [2.2]paracyclophane-containing conjugated compound consisting of 1,3,5-tris[(2,5-dimethylphenyl)ethynyl]benzenes. The compound exhibited a unique absorption band (cyclophane band) and emission from the phane state, both of which were the result of the π–π stacking of the poorly extended conjugation systems of 1,3,5-tris[(2,5-dimethylphenyl)ethynyl]benzene. We have prepared a CMP, in which 1,3,5-tris[(2,5-dimethylphenyl)ethynyl]benzenes were stacked. The CMP exhibited a type I nitrogen gas sorption profile and an H4-like hysteresis loop, and possessed the slit-like mesopores with a BET surface area of 501 $m^2\,g^{-1}$. This [2.2]paracyclophane-based CMP showed a morphology that was different from that of the benzene-based CMP. The effect of the [2.2]paracyclophane moiety on the CMP is currently under investigation. The synthesis, characterization, and properties of [2.2]paracyclophane-based CMPs will be reported in near future.

Acknowledgments

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Supplementary data

Supplementary data (synthetic details, ^1H and ^{13}C NMR spectra) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.08.067.

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13. Although CMP **P2** has already been synthesized, we prepared it from **3** with 1,4-diethynylbenzene. The S_{BET} value of **P2** we synthesized was 822 $m^2\,g^{-1}$. The ^{13}C NMR CP MAS and FTIR spectra (Figs. S14 and S15), SEM image (Fig. S15), XRD pattern (Fig. S19), and nitrogen adsorption–desorption isotherm (Fig. S20) of **P2** are shown in Supplementary data.
14. The morphology of **P2** we synthesized (Fig. S17) was also almost identical to the reported one; see Ref. 11a.