Sterically crowded hydrogen-bonded hexagonal network frameworks†
Ichiro Hisaki, Nobuaki Ikenaka, Seiji Tsuzuki and Norimitsu Tohnai

A hydrogen-bonded hexagonal network (H-HexNet) composed of C₃-symmetric π-conjugated molecules with six carboxyphenyl groups is one of the candidate platforms for porous organic materials. For formation of H-HexNets, a triangular cyclic structure, a so-called phenylene triangle (PhT) motif, composed of hydrogen-bonded carboxyphenyl groups is a key structure. In this paper, we synthesized two derivatives of hexakis(carboxyphenyl)triphenylene (TpMe and TpF, in which substituents (Me or F) were introduced in the ortho-positions of the carboxy groups, to investigate whether the PhT motif forms and how the structure and property of H-HexNets are affected by steric bulkiness around the hydrogen bonding moieties. Crystal structures, thermal stability, evaluation of permanent porosity by gas sorption experiments, and photochemical properties are revealed, which can contribute to establishment and fine-tuning of porous organic materials based on H-HexNets.

Introduction

A hydrogen-bonded (H-bonded) dimer of carboxy groups is one of the simplest and the most well-known supramolecular synthons, that is, structural units within supermolecules which can be formed and/or assembled by known or conceivable synthetic operations involving intermolecular interactions. The dimer, however, has been still an attractive H-bonding unit to achieve predesigned supramolecular architectures, due to its highly directional bonding nature and facile accessibility to a huge number of its derivatives.

Two dimensionally networked porous frameworks based on organic molecules have been intensively investigated from the viewpoints of not only gas storage and separation, catalysts and sensors, but also photoelectronic and (semi)conducting materials. They include metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and H-bonded organic frameworks (HOFs). Introducing the carboxy groups into building block molecules with a well-defined geometry can yield such HOFs. The pioneering system is the 2D honeycomb framework of trimesic acid, reported by March and Herbstein. Kobayashi also reported the layered assembly of a H-bonded hexagonal network (LA-H-HexNet) composed of hexakis(4-carboxyphenyl)benzene. Recently, some HOFs with permanent porosity have been constructed with carboxylic acid. However, it is still challenging to establish a general way to access functional HOFs with tunable pore size, shape, and surface properties.

In connection with this, we have also demonstrated that a series of C₃-symmetric planar π-conjugated hydrocarbons, such as triphenylene (Tp), possessing three 4,4′-dicarboxy-4-terphenyl moieties in the periphery form a dual-pored HexNet through a cyclic H-bonded motif called a phenylene triangle (PhT) (Fig. 1c), and that the H-HexNet stacks without inter-penetration to give layered HOFs (LA-H-HexNets) with porosity (Fig. 1a).

The important structural feature of the building block is that the peripheral carboxy phenyl groups are not coplanar but twisted against the plane of the central core (Fig. 1d, left). This twisted conformation enhances the solubility of the molecules in common organic solvents, provides shape-persistent pores surrounded by rigid phenylene walls, and plays a role in the stacking ways of H-HexNets to give layered structures.

In this study, we newly introduced substituents (Me or F) in the ortho-positions of the carboxy groups to force the carboxy and phenylene groups twisted (Fig. 1d, right), and investigated the effects of the substituents on molecular assemblies and properties. Regarding the steric effects of substituents on H-bonding, Os´mialowsky demonstrated that bulkiness of substituents near the H-bonding moiety can both increase and decrease attractive interactions, depending on the situation. Thus, understanding of steric effects on H-bonding is essential for constructing molecular architectures. Furthermore, in the case of a fluorine substituted derivative, electrostatic repulsion between oxygen and fluorine atoms might also have an effect on molecular conformation and packing.
Herein, we describe the synthesis of hexakis(4-carboxy-3,5-dimethylphenyl)triphenylene \( \text{TpMe} \) and hexakis(4-carboxy-3,5-difluorophenyl)triphenylene \( \text{TpF} \) (Fig. 1b), crystal structures of their LA-H-HexNets, their thermal stability, evaluation of their permanent porosity by gas sorption experiments, and their photochemical properties. We revealed, for the first time, how the structure and property of H-HexNets are affected by sterically twisted conformation and bulkiness of the peripheral hydrogen bonding moieties.

**Experimental**

**General**

\(^1\)H and \(^13\)C NMR spectra were measured using a Bruker (600 MHz for \(^1\)H, 150 MHz for \(^13\)C) or JEOL (400 MHz for \(^1\)H, 376 MHz for \(^13\)F) spectrometer. Residual \(^1\)H and \(^13\)C of the deuterated solvents were used as an internal standard [CDCl\(_3\): 7.27 ppm and DMSO-\(d_6\): 2.50 ppm for \(^1\)H, CDCl\(_3\): 77.00 ppm and DMSO-\(d_6\): 39.51 ppm for \(^13\)C]. For \(^19\)F NMR, 0.05%-C\(_6\)H\(_5\)CF\(_3\) in C\(_6\)D\(_6\) was used as an external standard (−62.0 ppm). Mass spectrum data were obtained from a JEOL JMS-700 instrument or Autoflex III Bruker. FT-IR spectra of the synthesized compounds were recorded using a JASCO FT/IR-4200 spectrometer. Thermogravimetric (TG) and differential thermal (DT) analyses were performed using a Thermo Plus 8120 (Rigaku) instrument under N\(_2\) purge at a heating rate of 5 °C min\(^{-1}\). Emission and excitation spectra in solid states were measured using a JASCO FP-6500 spectrofluorometer. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Ultima-IV using graphite-monochromatized Cu-K\(_\alpha\) radiation (\(\lambda = 1.54187 \text{ Å}\)) at room temperature. Gas sorption measurements were performed on Belsorp-max.

### Single crystal X-ray analysis

For crystals \( \text{TpMe-1}, \text{TpMe-3}, \text{and TpF-1} \), diffraction data were collected on a two-dimensional X-ray detector (PILOTUS 200K/R) equipped in a Rigaku XtaLAB P200 diffractometer using multilayer mirror monochromated Cu-K\(_\alpha\) radiation (\(\lambda = 1.54187 \text{ Å}\)). The cell refinements were performed with the software CrysallisPro 1.171.34.10.\(^{16}\) For crystals \( \text{TpMe-2}, \) diffraction data were collected on a CCD (MX225HE, Rayonix) with synchrotron radiation (\(\lambda = 0.8000 \text{ Å}\)) monochromated by the fixed exit Si (111) double crystal. The cell refinements were performed with HKL2000 software.\(^{17}\) Direct methods (SHELX)\(^{18}\) were used for the structure solution of the crystals. All calculations were

**Table 1  Crystal data of \( \text{TpMe-1}, \text{TpMe-2}, \text{TpMe-3}, \text{and TpF-1} \)**

<table>
<thead>
<tr>
<th>Formula</th>
<th>( \text{TpMe-1} )</th>
<th>( \text{TpMe-2} )</th>
<th>( \text{TpMe-3} )</th>
<th>( \text{TpF-1} )</th>
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<td>( \text{C}<em>{72}\text{H}</em>{60}\text{O}_{12} )</td>
<td>( \text{C}<em>{72}\text{H}</em>{60}\text{O}_{12} )</td>
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performed with the observed reflections \([I > 2\sigma(I)]\) with the program CrystalStructure crystallographic software packages,\(^{19}\) except for refinement which was performed by SHELXL.\(^{20}\) All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters. The SQUEEZE function equipped in the PLATON program was used to remove disordered solvent molecules in voids.\(^{21}\) Crystal data are listed in Table 1.

**Variable temperature (VT) PXRD measurements**

The crystalline bulk placed on an aluminum substrate was subjected to VT-PXRD measurements under the air atmosphere. PXRD data were collected on a Rigaku Ultima-IV using graphite-monochromatized Cu-K\(\alpha\) radiation (\(\lambda = 1.54187 \text{ Å}\)). The temperature of the sample was increased from room temperature to 360 °C at a rate of 1 °C min\(^{-1}\). During the temperature increase, XRD patterns ranging from 3° to 18° were repeatedly recorded with a scan rate of 3° min\(^{-1}\). Therefore, one PXRD scan has a temperature width of 5 °C.

**Ab initio calculations**

The geometries of 1-H, 1-Me, and 1-F (Chart 1) and their hydrogen bonded dimers were optimized at the MP2/6-311G** level using the Gaussian 09 program.\(^{22}\) Vibration analysis showed that the optimized structures are energy minimum structures. Conformational energies were calculated at the MP2/6-311G** level. The intermolecular interaction energies \(E_{\text{int}}\) were calculated at the MP2/cc-pVTZ level by the supermolecule method.\(^{23}\) The stabilization energy for forming a dimer from the isolated monomers \(E_{\text{st}}\) was calculated as the sum of the increase in energy due to the deformation of the monomers during formation of the dimer. Here, \(E_{\text{st}}\) was calculated at the MP2/cc-pVTZ level.

**Synthesis**

**Hexakis(4-methoxycarbonyl-3,5-dimethylphenyl)triphenylene derivative 4.** A mixture of 2,3,6,7,10,11-hexabromotriphenylene (52.6 mg, 75.0 μmol), 3,5-difluoro-4-methoxycarbonylphenylboronic acid pinacolyl ester 3 (166 mg, 0.551 mmol), PdCl\(_2\)(dppf) (31.3 mg, 31.1 mmol), and Na\(_2\)CO\(_3\) (81.5 mg, 0.769 mmol) in deoxygenated toluene (10 mL) and water (5 mL) was stirred for 40 h under reflux conditions. The precipitate was filtered and washed with CHCl\(_3\). The product was dissolved in acetone, followed by the addition of hexane, yielding pure TpMe. The product was dissolved in acetone, followed by the addition of hexane, yielding pure TpMe.

**Results and discussion**

**Theoretical calculation of hydrogen bonding**

To investigate the \textit{ortho}-substitution effects on the structures and magnitude of the interactions of the hydrogen bonded dimer,
three model systems 1-H, 1-Me, and 1-F were subjected to theoretical calculation (Chart 1). In contrast to 1-H, which has a coplanar conformation \((\omega = 0^\circ)\), where \(\omega\) denotes dihedral angles between the benzene ring and the carboxy group, 1-Me and 1-F have a twisted conformation \((\omega = 53.8^\circ\) and 54.5°, respectively) due to steric hindrance of the substituents. The co-planar conformers of 1-Me and 1-F are less stable than the corresponding twisted energy minimum conformers by as much as 2.37 kcal mol\(^{-1}\) and 1.86 kcal mol\(^{-1}\), respectively. The 1-Me and 1-F dimers have two nearly isoenergetic isomers shown in Fig. S1 (ESI†). The energy differences between the isomers are less than 0.1 kcal mol\(^{-1}\).

Subsequently, the \(E_{\text{form}}\) for the dimers of 1-H, 1-Me, and 1-F was calculated (Table 2). Stabilization energies of the dimers of 1-H, 1-Me, and 1-F range from −14.8 to −15.4 kcal mol\(^{-1}\), indicating that substituent effects on hydrogen bonding energy are negligible. This result is consistent with the atomic charges on carboxyl oxygen atoms and hydrogen atoms of the carboxy group in 1-H, 1-Me, and 1-F obtained by ab initio calculations (Table S2, ESI†). The charges on these atoms are nearly identical in the three molecules, in spite of the different \(\sigma\)-substituents. To further elucidate the substituent effects on the hydrogen bonds of the carboxy group, we evaluated the interactions of carboxylic acids (1-H, 1-Me, 1-F) with \(\text{Na}^+\) and \(\text{Cl}^-\) as shown in Fig. S2 and S3 (ESI†). No significant differences were observed among the interactions of these three carboxylic acids with \(\text{Na}^+\) and \(\text{Cl}^-\).

### Synthesis and crystallization of TpMe and TpF

Hexakis(methoxycarbonylphenyl)triphenylene derivatives 4 and 5 were synthesized in 64% and 37%, respectively, by Suzuki–Miyaura cross coupling of 2,3,6,7,10,11-hexabromotriphenylene and the corresponding boronic acid 2 or pinacol borate 3 in the presence of \(\text{Pd(dppf)}\text{Cl}_2\) and bases. Subsequently, hydrolysis of 4 and 5 was performed with \(\text{CF}_3\text{CO}_2\text{H}\) and \(\text{KOH}\), respectively, to yield TpMe and TpF in 64% and 85% yields, respectively (Scheme 1a).

TpMe and TpF were recrystallized by slow evaporation of a mixed solution of DMF and methyl benzoate at 50 °C to yield single crystals suitable for X-ray crystallographic analysis (Scheme 1b). TpMe yielded totally three polymorphic crystals TpMe-1, TpMe-2, and TpMe-3 under the same conditions. However, it needs to be mentioned that it is not clear whether three polymorphs are always contained in the crystalline bulk formed in the same batch, because a general diffractometer in the laboratory provided only weak and ambiguous XRD patterns for the obtained crystalline materials due to the low electron density contrast generated by disordered methyl benzoate molecules within the pores, making it difficult to characterize the polymorphic forms. Therefore, such bulk crystals obtained by crystallization at 50 °C are called TpMe-2Ds. On the other hand, TpF yielded one crystalline form TpF-1.

### Crystal structures of HexNet frameworks

In the crystal structures of TpMe-1, TpMe-2, and TpMe-3 (Fig. 2), TpMe forms a H-HexNet, which stacks in a non-interpenetrated manner to give layered assemblies (LA-H-HexNets). TpMe-1 shows conformational disorder at five carboxy groups due to steric hindrance of the \(\sigma\)-substituents as shown by yellow atoms in Fig. 2a. This kind of rotational disorder was expected, as predicted by the theoretical calculation. However, to our surprise, the other polymorphs show no rotational disorder at the carboxy groups, and furthermore, all three polymorphs have no disorder at the phenylene groups, although their anisotropic displacement ellipsoids are more extended compared with those of the triphenylene core. The void ratios in TpMe-1, TpMe-2, and TpMe-3 are 45.2%, 35.9%, and 41.5%, respectively, which are relatively small compared with LA-H-HexNets of Tp (50.0–54.4%) due to the bulky substituents.\(^{12}\) In the void spaces, methyl benzoate molecules are accommodated, although they are severely disordered.

The present polymorphs were caused by versatile conformations of the phenylene groups and slightly different stacking manners of the HexNet sheets. To evaluate the conformational versatility of the peripheral carboxy phenyl moieties, the following two parameters \(\phi\) and \(\omega\) were introduced (Fig. 3), where \(\phi\) denotes the dihedral angle between the triphenylene core and the phenylene ring and \(\omega\) denotes the dihedral angle between the phenylene ring and the carboxy group. The values are listed in Table 3. As we expected, dihedral angle \(\phi\) in the TpMe polymorphs ranges from −75.8° to +55.7°, which is similar to that of Tp-1. On the other hand, dihedral angle \(\omega\) in the TpMe

<table>
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<th>Dimer</th>
<th>(E_{\text{int}}^a)</th>
<th>(E_{\text{def}}^b)</th>
<th>(E_{\text{form}}^c)</th>
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<tr>
<td>1-H</td>
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<td>−15.4</td>
</tr>
<tr>
<td>1-F</td>
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<td>2.3</td>
<td>−14.8</td>
</tr>
<tr>
<td>1-Me</td>
<td>−17.7</td>
<td>2.5</td>
<td>−15.2</td>
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</table>

\(E_{\text{int}}\) is the intermolecular interaction energy calculated for the hydrogen bonded dimer at the MP2/cc-pVTZ level. \(E_{\text{def}}\) is the deformation energy. \(E_{\text{form}}\) is the stabilization energy for the formation of a dimer, which is the sum of \(E_{\text{int}}\) and \(E_{\text{def}}\). See text for details.
polymorphs ranges from \(-87.0^\circ\) to \(+84.9^\circ\), which is significantly larger compared to that of \(\text{Tp-1}\) (i.e. \(-4.3^\circ\) to \(+11.5^\circ\)).

In contrast to \(\text{TpMe}\), \(\text{TpF}\) has yielded one crystalline form \(\text{TpF-1}\) under the same crystallization conditions as with \(\text{TpMe}\) (Fig. 4).

In the crystal structure, the \(\text{TpF}\) molecule with a two-fold axis forms a LA-H-HexNet with a stacking manner similar to that of \(\text{TpMe-1}\). The void ratio of \(\text{TpF-1}\) is 50.4% and severely disordered methyl benzoate molecules are accommodated in the void. Interestingly, all the phenylene groups and four of six carboxy groups are rotationally disordered into two positions and their anisotropic displacement ellipsoids are also elongated. The phenylene rings of the molecule in \(\text{TpF-1}\) are twisted as observed in other \(\text{TpMe}\) and \(\text{Tp-1}\) systems (see \(\psi\) values in Table 3). The carboxy groups are also twisted against the plane of the phenylene rings: \(\omega\) values range from \(-80^\circ\) to \(-90^\circ\).
Although the exact values are not presented due to the relatively severe disorder of the carboxy groups.

Versatile conformations of TpMe and TpF observed in crystalline states can be explained by the following interpretation. Namely, introduction of substituent groups into the ortho-positions of the carboxy group causes an increase of the rotationally variable range of the carbonyl groups, in addition to the phenylene groups. This wide range of conformations results in the generation of three polymorphs in the case of TpMe. However, the conformation of the TpMe molecule is fixed in one way in each of the polymorphs due to the bulkiness of the methyl group. In the case of TpF, on the other hand, the varied conformation of the peripheral groups causes no polymorphs but one crystalline form with significant disordered peripheral hydrogen-bonding groups (Fig. 4b). Probably, fluorine atoms at the ortho-positions are not bulky enough to affect the molecular packing and generation of polymorphs, and the varied rotational ability of the peripheral groups is neutralized by local rotational disorder.

**Thermal behaviour of the frameworks**

Freshly prepared crystalline bulks of TpMe-2Ds (which contain either one, two, or all forms of TpMe-1, TpMe-2, and TpMe-3) and TpF-1 were subjected to thermal analysis (Fig. 5). The thermogravimetric (TG) curve of TpMe-2Ds revealed that the included solvent was completely released at around 200 °C. The weight loss of 38 wt% indicates that the framework involved solvent molecules (methyl benzoate) with a host–guest ratio of 1:4, which is also supported by 1H NMR spectroscopy (Fig. S4 and S5, ESI†). The second weight loss starting from ca. 300 °C is assigned to thermal decomposition of the compound. TpF-1, the host–guest ratio of which is 1:7 (47 wt%) based on 1H NMR spectroscopic analysis (Fig. S5, ESI†), showed ambiguous TG curves involving several steps of the weight loss. Removal of the guest molecules and thermal decomposition may occur simultaneously.

To obtain structural information during desolvation by heating, powder X-ray diffraction (PXRD) patterns of crystalline bulks of TpMe-2Ds and TpF-1 were recorded with gradual heating (Fig. 6). The initial patterns are not clear, particularly in the case of TpMe-2Ds, due to the severe disorder of solvent molecules accommodated in voids. However, peaks gradually appeared upon heating.

Upon heating of TpMe-2Ds, obvious peaks started to grow at 4.54°, 5.18°, 7.96° and so on at 116 °C and plateaued at around 190 °C. The obtained pattern is not in agreement with the simulated pattern of either TpMe-1, TpMe-2, or TpMe-3, indicating that structural changes occurred. Complete removal of the solvent molecules was confirmed by 1H NMR spectroscopy. The pattern then started to change at 301 °C and completely disappeared at around 347 °C due to thermal decomposition of the compound.

In the case of TpF-1, the pattern change occurred in three steps, although the signal/noise ratio was relatively low. First, new peaks started to appear at around 6.9° and 7.2° at 55 °C. Then, other new peaks at 5.4° and 8.1° started to appear at 115 °C. Finally, the remaining peaks started to decay at around 155 °C and any peaks that remained disappeared at around 200 °C. This indicates that the TpF-1 crystal changes into an amorphous phase by heating or desolvation via two intermediate phases. These multi-step structural changes are also implied by the TG curve (Fig. 5b).

In this way, despite the fact that both compounds have similar molecular structures and form similar LA-H-HexNets, their structure-retention ability strongly depends on the substituents at the ortho-positions. Particularly, it was revealed that the HexNet framework of TpF-1 is not resistant to heat higher than ca. 150 °C.

Activation (desolvation with retaining pores) of TpMe-2Ds and TpF-1 crystalline bulks was preliminarily attempted by heating at 100 °C or 200 °C under vacuum conditions, resulting in a significant loss of crystallinity in the case of both TpMe-2Ds and TpF-1 at both temperatures. Consequently, activation was performed by a solvent exchange method. The PXRD pattern of as-formed crystalline bulks of TpMe again shows an ambiguous profile (Fig. 7a-ii), which is therefore difficult to be characterized when compared with the simulated pattern of TpMe-1, TpMe-2, and TpMe-3 (Fig. 7i-1, i-2 and i-3, respectively). The as-formed crystalline bulk of TpMe-2Ds was soaked in benzene solution to exchange the solvent molecules in the pores. After soaking for 48 h, we confirmed by 1H NMR spectroscopy that methyl benzoate was completely replaced with benzene (Fig. S6, ESI†). The resultant material showed an obvious PXRD pattern (Fig. 7a-iii). Subsequently, the materials were laid under vacuum conditions at 60 °C for 24 h, enabling complete desolvation to yield crystalline porous material TpMe-apo (Fig. 7a-iv and Fig. S7, ESI†).
The PXRD pattern of TpMe-apo is in good agreement with that observed in VT-PXRD analysis (Fig. 6a).

Activation of TpF-1 was performed by the same procedure as in the case of TpMe-2Ds except for the complete removal of benzene, which needed additional heating at 100 °C for another 24 h under vacuum conditions, to yield a desolvated material TpF-apo (Fig. S8–S10, ESI†). However, the crystallinity of the resultant TpF-apo was very low (Fig. 7b-iv).

Gas sorption properties

To evaluate the permanent porosity of TpMe-apo and TpF-apo, N₂, CO₂, and H₂ adsorption–desorption experiments were undertaken at 77 K, 195 K, and 77 K, respectively (Fig. 8). TpMe-apo shows a type-I sorption isotherm for all gasses, indicating that TpMe-apo has micropores within the framework. The amounts of uptake for N₂, CO₂, and H₂ are 182 cm³ g⁻¹, 157 cm³ g⁻¹, and 81 cm³ g⁻¹, respectively. The pore size distribution of TpMe-apo was calculated by the nonlocal density functional theory (NL-DFT) method (Fig. S11, ESI†), resulting in a diameter of 0.77 nm, which is in good agreement with the pore size provided by layered HexNet frameworks composed of triphenylene derivatives (Tp-apo). Indeed, the amounts of uptake and sorption selectively for gas species are quite similar between TpMe-apo and Tp-apo. TpF-apo shows quasi type-I sorption isotherms for CO₂ with an uptake of 91 cm³ g⁻¹, while it shows almost no adsorption for N₂ and H₂. This result, combined with PXRD changes upon heating, indicates that TpF-apo does not retain the LA-H-HexNet structure but is a less crystalline material with narrower void spaces. The surface area (SBET) calculated by the Brunauer–Emmett–Teller model for CO₂ sorption isotherms is 561 m² g⁻¹ for TpMe-apo and 219 m² g⁻¹ for TpF-apo. It is noteworthy that TpF-apo exhibits selective sorption behavior for CO₂, mainly due to the size effect of the narrow pores, and presumably due to the additional electrostatic effects of fluorine substituents, although the contribution of the latter effect is small.25

Fluorescence properties in solid states

The photochemical properties of LA-H-HexNets of TpMe and TpF were investigated before and after desolvation. Fig. 9 shows the fluorescence and excitation spectra of the as-formed crystals (TpMe-2Ds and TpF-1) and the corresponding desolvated materials (TpMe-apo and TpF-apo). TpMe-2Ds exhibits a structureless emission band at 407 nm ($\phi_f = 0.17$, where $\phi_f$ denotes the fluorescence quantum yield), which was slightly red-shifted by 4 nm after desolvation ($\phi_f = 0.09$ for TpMe-apo). Excitation spectra are also red-shifted from 373 nm to 388 nm, indicating that intermolecular interactions between the adjacent triphenylene cores in TpMe-apo are stronger than those in TpMe-2Ds. TpF-apo also exhibits a structureless emission band at 423 nm ($\phi_f = 0.23$), which was red-shifted by 12 nm compared with TpF-1 ($\phi_f = 0.16$). The excitation maxima of TpF-1 and TpF-apo are 381 nm and 394 nm, respectively.

Conclusions

In this paper, we synthesized two derivatives of hexakis(carboxyphenyl)triphenylene TpMe and TpF, in which substituents (Me or F) were introduced in the ortho-positions of the carboxy groups, and investigated the substituent effects on the crystal structures of the LA-H-HexNets, thermal stability, and retention ability of permanent porosity. As a result, we revealed the following important features of the present system. (1) Substituent groups have no effects on the binding energy of hydrogen-bonded dimerization (~15 kcal mol⁻¹). (2) Methyl and fluorine...
substituents in the ortho-positions of the carboxy groups made both carboxy and phenylene groups twisted, resulting in an increase of variability of peripheral conformation. (3) Depending on the bulkiness of the substituents, TpMe yielded three polymorphs, while TpF yielded one crystalline form with highly disordered peripheral groups. (4) Thermal stability and permanent porosity were drastically changed by the substituents despite the fact that both the crystals have quite similar LA–H-HexNet structures. These results can contribute to the development of functional HOFs with tunable pores based on H-HexNet frameworks.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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