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## ARTICLE

## A hydrogen-bonded organic framework possessing one-dimensional wide channels surrounded by naphthalenediimide plane

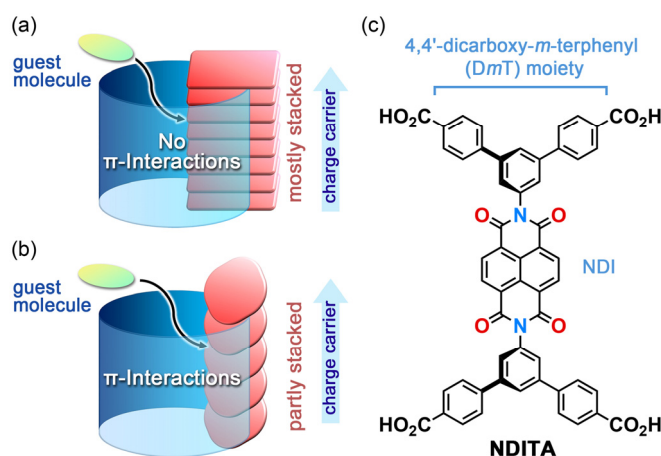
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$\pi$ -Conjugated molecule-based porous organic frameworks that possess both one-dimensionally  $\pi$ -stacked columnar domains and pore channels surrounded by the  $\pi$ -conjugated surface are a sophisticated platform for optoelectronic materials responsive to chemical stimuli. In this paper, we report a hydrogen-bonded organic framework (HOF) with a wide inclusion channel whose surfaces are composed of the  $\pi$ -conjugated plane of naphthalenediimide (NDI). Brunauer–Emmett–Teller surface area was determined to be 1410 m<sup>2</sup> g<sup>-1</sup>. Slipped-stacking of a hydrogen-bonded two-dimensional network composed of tetracarboxylic acid **NDITA** with an NDI core provides both electron-conductive  $\pi$ -stacked NDI domains and pore channels surrounded by the NDI surface. Since aromatic solvents can come into contact with the NDI moieties in the pores, the HOF exhibits solvent-dependent photophysical behaviors. Particularly, inclusion of dimethoxybenzene (DMB) into the pores enhances charge-transfer interactions, resulting in significant changes in absorption and emission spectra as well as electron conductivity.

## Introduction

Two-dimensionally networked porous frameworks constructed from  $\pi$ -conjugated molecules, such as metal-organic frameworks (MOFs)<sup>1–4</sup> and covalent organic frameworks (COFs),<sup>5–8</sup> are attracting interest as promising candidates for semiconductors, photocatalysts, and electrocatalysts. Well overlapped two-dimensional (2D) network sheets can provide both columnar domains formed by  $\pi$ – $\pi$  stacking of the  $\pi$ -conjugated cores and one-dimensional (1D) pores along the stacking directions. The former can serve pathway for charge carriers, and the latter allows guest molecules access from outside the framework through the channels. However, such  $\pi$ -stacked structures prevent aromatic guest molecules from interacting with the  $\pi$ -orbitals of the building block molecules, resulting in poor guest-responsivity of electronic properties (Fig. 1a). To achieve efficient host-guest interactions, the channel walls of the framework should be composed of  $\pi$ -conjugated surfaces.<sup>9,10</sup> Such frameworks can be achieved using non-coplanar and robust molecules, including triptycene



**Fig. 1** Porous frameworks with (a) mostly stacked and (b) partly stacked  $\pi$ -conjugated building block molecules. (c) Bis(4,4'-dicarboxy-*m*-terphenyl)naphthalenediimide (**NDITA**).

derivatives.<sup>11–14</sup> In the system, on the other hand, no pathway for charge transport is formed. Therefore, the framework is required to exhibit both the channel surrounded by  $\pi$ -conjugated planes and the  $\pi$ -stacked columnar structure. In this context, the porous framework formed by partially stacked  $\pi$ -conjugated molecules meets the above requirements (Fig. 1b).

For precise structural characterization of the porous frameworks, those formed through reversible bonds, such as dynamic covalent bonds<sup>15</sup> and hydrogen bonds, are preferable because of their single crystallinity suitable for single-crystal X-ray diffraction (SCXRD) analysis. Particularly, hydrogen-bonded

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organic frameworks (HOFs) have been intensively investigated from this point of view,<sup>16–25</sup> although excellent single-crystalline COFs are also reported recently<sup>26–28</sup>.

Naphthalenediimide (NDI) is one of the most typical n-type semiconductor molecules, and NDI-based MOFs<sup>29</sup> and COFs<sup>30,31</sup> have been actively researched from the perspectives of redox and photoelectronic properties.<sup>32,33</sup> On the other hand, only a handful of NDI-based HOFs were reported.<sup>34–42</sup> Luo and coworkers reported a photochromic and electrochromic HOF based on NDI.<sup>34</sup> Ono, Mathevet, Adachi and coworkers reported an electron-conductive HOF using a cyclopentanol-modified NDI derivative.<sup>37</sup> Champness and coworkers reported photoinduced radical formation of NDI-based HOFs.<sup>41</sup> Nevertheless, electron-conductive, stimuli-responsive NDI-HOFs with large void spaces are unexplored.

In this study, we report on the structure and properties of NDI-based HOF that possesses large voids. The HOF **NDITA-1** is composed of bis(4,4'-dicarboxy-*m*-terphenyl)naphthalenediimide (**NDITA**), a derivative of NDI modified with 4,4'-dicarboxy-*m*-terphenyl (*DmT*) moieties (Fig. 1c). Since **NDITA** has an orthogonal conformation between the *DmT* and NDI moieties, slip-stacking of the molecule resulted in formation of a layered HOF that possesses  $\pi$ -stacked columnar domains and pore channels surrounded by  $\pi$ -conjugated planes. These structural factors allowed the HOF to exhibit electron conductivity through the stacked NDI parts and aromatic guest responsivity due to interactions between the exposed NDI plane and the guests. These results suggest that the HOF with  $\pi$ -conjugated moieties partially exposed to the pore surface and partially stacked with neighboring  $\pi$ -conjugated moieties is a promising platform to develop materials that enable the

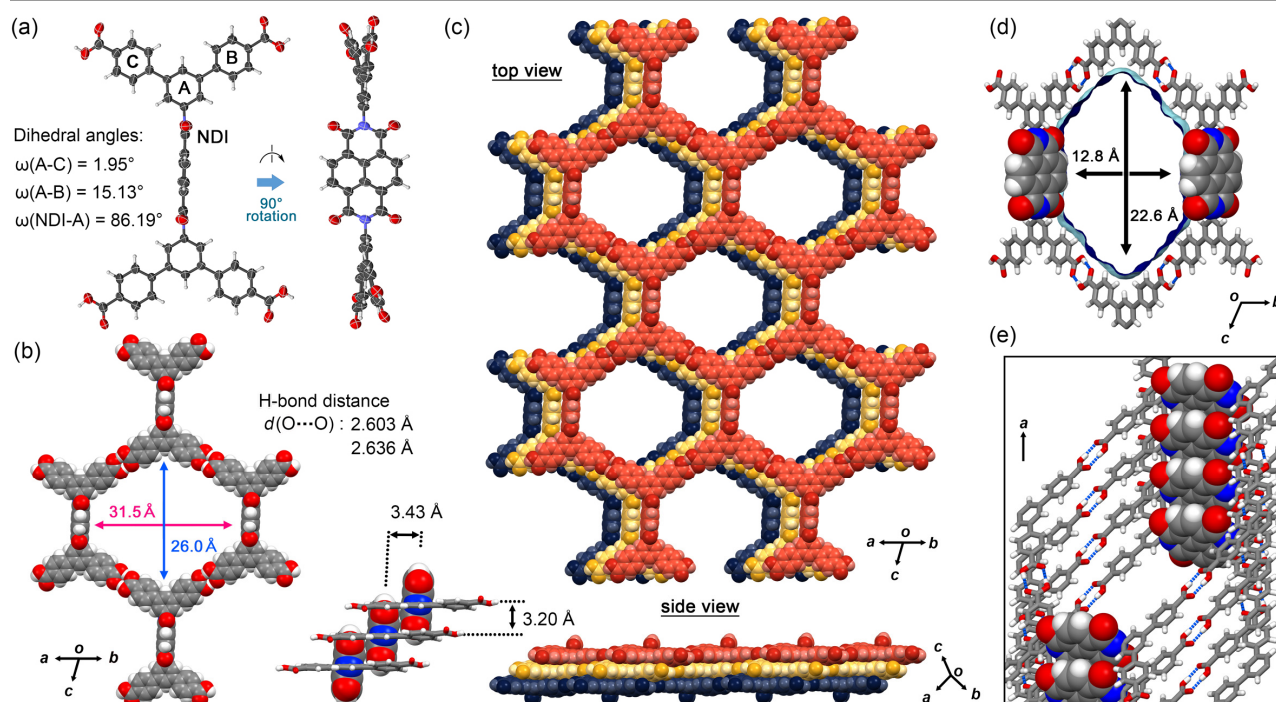
dynamic modulation of electronic properties by guest molecules.

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## Results and discussion

### Crystallography of HOF NDITA-1

**NDITA** was synthesized according to the literature (Scheme S1 and Fig. S1).<sup>43,44</sup> The synthesized compound was recrystallized by slow evaporation of a solution of **NDITA** dissolved in *N,N'*-dimethylformamide (DMF) and 1,2,4-trichlorobenzene (TCB) at 140 °C, yielding solvated HOF **NDITA-1**(TCB) as needle crystals with an average dimension of 10  $\mu\text{m}$   $\times$  10  $\mu\text{m}$   $\times$  150  $\mu\text{m}$  (Fig. S2). The first attempt was made to perform SCXRD analysis using an in-house diffractometer equipped with a Cu-tube. However, the analysis failed because of only a small number of weak diffraction peaks. Consequently, the crystal structure of the HOF was successfully revealed using the focused and high-flux synchrotron X-ray radiation (Fig. 2 and Table S1). A **NDITA** molecule with the inversion center crystallized into the space group *P*-1. The *DmT* moieties have nearly planar conformation due to packing forces in the crystal: dihedral angles between the central benzene ring (A) and the peripheral rings (B and C) are 15.1° and 2.0°, respectively (Fig. 2a), which significantly differ from the theoretically optimized structure (Fig. S4 and Table S2). The NDI core and *DmT* moieties have almost orthogonal arrangements: the dihedral angle between the ring A and NDI is 86.2°. The orthogonal conformation was frequently observed in other crystalline systems of diaryl NDI derivatives.<sup>29–33</sup> **NDITA** form a honeycomb-like *sql*-topological network sheet through intermolecular H-bonded dimerization of the peripheral



**Fig. 2** Crystal structure of HOF **NDITA-1**(TCB). (a) Molecular conformation with nearly orthogonal fashion. (b) Motif of *sql*-network. (c) Selected layered structure composed of three sheets. (Inset) Interlayer distances between the *sql*-sheets and those between NDI cores. (d) Visualized surfaces of the solvent accessible void. (e) The channel wall composed of the  $\pi$ -conjugated plane of NDI.



carboxy groups: the O...O distances are 2.64 and 2.60 Å (Fig. 2b). The resultant sheet structure has a hexagonal aperture with the dimensions of 26.0 Å × 31.5 Å. The sheets are slip-stacked with an interlayer distance of 3.20 Å, resulting in a layered framework with 1D channel spaces with an aperture size of 22.6 Å × 12.8 Å (Fig. 2c,d). It is noteworthy that two of the six inside walls of the channel are composed of the NDI molecular plane. By stacking 2D sheets, a half part of the  $\pi$ -conjugated plane of NDI overlaps with the adjacent  $\pi$ -plane of NDI with an intermolecular distance of 3.43 Å, and the other half part is exposed within the channel. Therefore, it is expected that guest molecules can approach the  $\pi$ -conjugated plane of NDI directly and add perturbation to the electronic state of **NDITA** in the HOF. In the channel, disordered solvent molecules (TCB) are accommodated with a host : guest ratio of 1 : 6 – 7 (Fig. S5). Void ratio of the solvent accessible volume was calculated to be 57.4% by PLATON with the probe radius of 1.2 Å.<sup>45</sup>

The present stacking manner is governed by the molecular geometry with the orthogonal conformation of the NDI and *DmT* moieties as well as effective CH/O interactions between the aromatic hydrogen atom of the *DmT* group and the oxygen atom of the NDI core (Fig. S3). This slip-stacking manner of **NDITA** in the HOF enables LUMO orbitals of the NDI core to have a preferable overlap with the same phase. However, no mixing of the MOs was observed (Figs. S11 and S12).

### Thermal stability

Thermal gravimetry (TG) analysis on bulk crystals of **NDITA-1**(TCB) shows weight loss of 60% by heating up to 200 °C due to the release of the guest molecules (Fig. 3a). Another weight loss observed at approximately 300 °C is probably due to thermal decomposition of the molecules. The structural changes of HOF **NDITA-1**(TCB) were monitored by variable-temperature

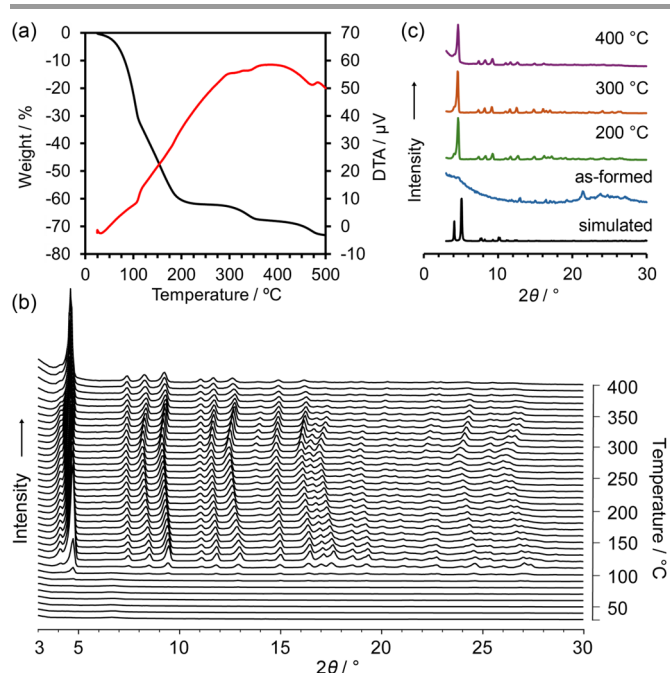
powder X-ray diffraction (VT-PXRD) analysis on the bulk crystals (Fig. 3b). An ambiguous profile was observed below 100 °C due to the significantly low electron diffraction contrast provided by the low density frameworks composed of light-weight elements and scattering of diffracted X-ray by disordered TCB molecules inside the channel, which is often observed for the solvated HOF crystals that include chlorinated aromatic solvent molecules.<sup>46,47</sup> Diffraction peaks start to appear at 100 °C, and become apparent at higher temperatures. The diffraction pattern is similar to that simulated from the SCXRD data, although they are not exactly matched. For example, characteristic peaks at 4.10°, 5.03°, and 5.11° corresponding to the (0 0 1), (0 1 0), and (0 1 -1) planes in the crystal structure of **NDITA-1**(TCB) were replaced by one prominent peak at 4.61° and a weak peak at 4.08°. These changes in the pattern were probably caused by the slight deformation of the framework by slipping of the layers during and/or after release of the guest solvent molecules. Single crystals of **NDITA-1**(TCB) heated at 130 °C under vacuum conditions retained needle-like crystalline morphology, while transparency was declining (Fig. S6), indicating subtle changes of the framework. We attempted SCXRD analysis using these activated crystals and the analysis using a PXRD pattern, both of which failed to give a precise crystal structure.

Upon further heating, the diffraction peaks were slightly shifted into the small-angle regions, and then shifted back to the wide-angle regions at temperatures higher than 300 °C. In more detail, some diffraction peaks, such as at 7.50°, 11.1° and 15.0° showed less shift than others, such as at 9.47°, 13.0° and 16.5°, indicating anisotropic structural deformation of the framework. The diffraction pattern remained even when heated up to 400 °C.

### Porosity

According to the thermal analysis described above, activation of HOF **NDITA-1**(TCB) was first attempted by heating under reduced pressure conditions. However, the resultant samples showed relatively weak diffraction peaks and only a subtle amount of gas uptake. Therefore, activation was conducted using supercritical fluid of carbon dioxide (for the detailed conditions, see ESI). The activated HOF **NDITA-1a** showed a diffraction pattern closer to that of **NDITA-1**(TCB) compared with that observed during the VT-PXRD measurements, indicating that the nearly original framework structure was retained (Fig. S7). The complete removal of guest solvent molecules was confirmed by <sup>1</sup>H NMR spectrum of the sample dissolved in DMSO-*d*<sub>6</sub> solution.

N<sub>2</sub> and CO<sub>2</sub> sorption experiments were conducted at 77 K and 195 K, respectively, using freshly activated samples (Fig. 4a). The N<sub>2</sub> adsorption isotherm exhibited a sharp rise at relative pressure (*P*/*P*<sub>0</sub>) below 0.01, followed by a small step, and reached a plateau at *P*/*P*<sub>0</sub> of 0.1. The uptake amount was 350 cm<sup>3</sup>(STP)g<sup>-1</sup> at *P*/*P*<sub>0</sub> of 0.9. Brunauer–Emmett–Teller (BET) surface area of **NDITA-1a** was calculated to be 1410 m<sup>2</sup> g<sup>-1</sup> (Fig. S8). CO<sub>2</sub> adsorption isotherms at 195 K exhibit a sigmoidal shape with a hysteresis at *P*/*P*<sub>0</sub> ~ 0.15, indicating that interactions



**Fig. 3** Thermal analysis of **NDITA-1**(TCB). (a) TG-DA curves. (b) VT-PXRD patterns. (c) Representative PXRD patterns of the VT experiment.





between the pore surface and CO<sub>2</sub> are less attractive or a certain structural change was derived by the adsorption. The total amount of uptake is 192 cm<sup>3</sup> (STP) g<sup>-1</sup>. The pore diameter was estimated using the non-local density functional theory (NLDFT) method for the N<sub>2</sub> adsorption isotherm shows a peak at 1.88 nm (Fig. 4b). Unfortunately, the sample after being subjected to gas sorption experiments showed a decrease in the diffraction intensity in the PXRD pattern and in the uptake amount of gas, indicating a fragile nature of the activated framework.

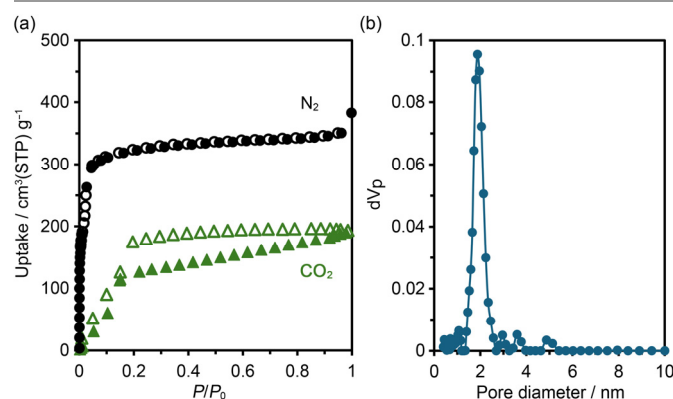


Fig. 4 (a) Gas sorption isotherms for N<sub>2</sub> at 77 K (black) and CO<sub>2</sub> at 195 K (green). (b) Pore width distribution using the NLDFT model for the N<sub>2</sub> adsorption isotherm.

### Guest solvent-dependent photophysical properties

**NDITA** shows absorption bands at 270, 360, and 380 nm in a DMF solution (Fig. 5). The observed lowest-energy band is attributed to the transition from HOMO-2 to LUMO at 383.9 nm ( $f = 0.629$ ), corresponding to the  $\pi$ - $\pi^*$  transition of the NDI moiety, according to the TDDFT calculation of **NDITA** (Figs. S9 and S10). On the other hand, the calculated HOMO-LUMO transition at 450.9 nm, which corresponds to an intramolecular CT transition from the *DmT* to NDI moieties, is symmetrically forbidden ( $f = 0.018$ ), and was not observed experimentally. A fluorescence spectrum shows a band at 436 nm.

Then, spectroscopic analyses on the aromatic guest molecule-included HOFs were conducted in a solid state. An amorphous solid of **NDITA** shows an absorption band at 380 nm with a broad shoulder from 450 to 650 nm (Fig. 6). The HOF activated using supercritical fluid of carbon dioxide also showed quite a similar absorption band with the amorphous solid (Fig. S13), indicating that the amorphous solid and activated HOF has similar molecular stacking orientation in short distance ranges. As-formed crystalline powder of **NDITA-1**(TCB) shows a band at ca. 450–500 nm originating from intermolecular interactions between the framework and TCB molecules. The guest-included HOFs were prepared by immersing bulk crystals of **NDITA-1**(TCB) in the corresponding solvents, affording exchange of the included guest molecules. When the HOF was immersed in *o*-dimethoxybenzene (DMB), an obvious color change from pale yellow to brown was observed. A diffused reflection spectrum of the DMB-immersed HOF shows a band at around 550 nm, which appeared lower energy region than for that of **NDITA-**

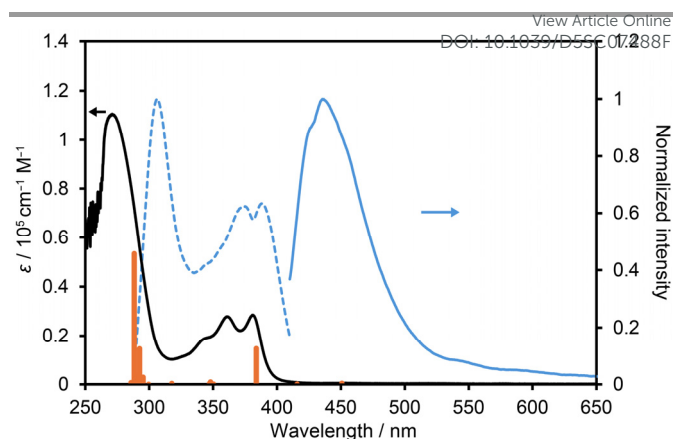
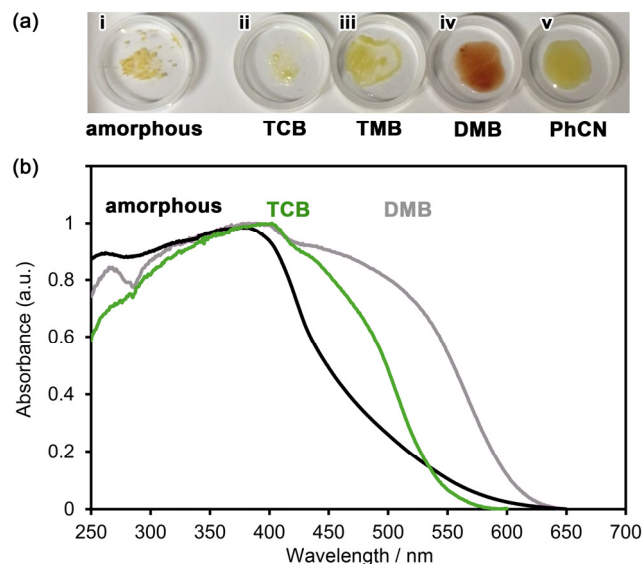


Fig. 5 Absorption (black solid line), fluorescence (cyan solid line), and excitation (cyan dotted line) spectra of **NDITA** in a DMF solution. Calculated one-electron transition oscillations are shown with orange bars in arbitrary units. The fluorescence spectrum was measured with the excitation wavelength of 381 nm. The excitation spectrum was recorded at 430 nm.

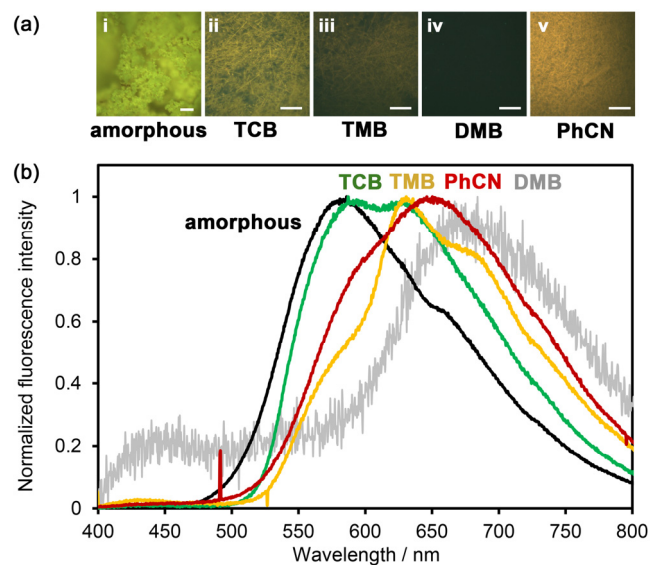
**1**(TCB) and the amorphous solid. The band was caused by charge transfer (CT) interactions between electron-deficient NDI and electron-rich DMB. Other solvents such as 1,2,4-trimethylbenzene (TMB) and benzonitrile (PhCN) showed no significant color changes.

The solvent-immersed HOFs also exhibit solvent-dependent fluorescence changes (Fig. 7), although the intensity is very weak: the fluorescence quantum yield is less than 0.5%. The amorphous solid exhibits an emission band at 583 nm accompanied by a shoulder at around 655 nm. The band is red-shifted by 147 nm compared to that in a DMF solution (Fig. 5). The as-formed HOF **NDITA-1**(TCB) showed two emission bands at 589 and 627 nm. TMB-immersed HOF showed emission maximum at 631 nm with shoulders at 580 and 680 nm. PhCN-immersed HOF exhibits a band at 650 nm with shoulder at 600 nm. The observed red-shifted band for PhCN-immersed HOF indicates the existence of attractive interactions presumably between the electron-rich *DmT* moieties of **NDITA** and the electron-deficient PhCN molecule. Although DMB-immersed HOF shows almost no emission (Fig. S14), the magnified emission spectrum shows a band at 680 nm, which is consistent with the formation of a CT complex.<sup>48</sup> It is reported that volatile organic compound (VOC)-induced fluorescence color changes of NDI-based porous coordination polymers (PCPs) are correlated with the ionic potential of VOC absorbed in the PCP.<sup>49,50</sup> In the present system, on the other hand, the relationship between the color changes and the ionization potential of the aromatic solvent is ambiguous, while Gutmann donor number may show better correlation with the emission maximum wavelength (Table S3). Bulk crystals of **NDITA-1**(TCB) immersed in the solvents were also subjected to PXRD measurements to confirm whether structural changes occurred or not upon the immersion (Fig. S15). The HOFs immersed in TMB, DMB, and PhCN showed obvious diffraction profiles similar to the activated sample and **NDITA-1**(TCB), although the diffraction of **NDITA-1**(TCB) is very weak due to TCB molecules being disordered in the pore, as we explained. It should be





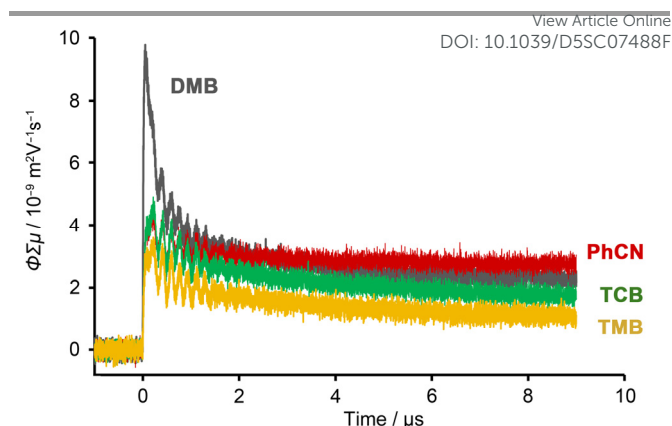
**Fig. 6** (a) Photographs of solvent-dropped bulk crystals of HOF CPNDI-1; (i) Amorphous solid, (ii) as-formed **NDITA-1**(TCB), (iii) TMB-immersed HOF, (iv) DMB-immersed HOF and (v) PhCN-immersed HOF. (b) Normalized diffuse reflection spectra of amorphous solid (black), **NDITA-1**(TCB) (green) and DMB-immersed HOF (grey). The spectra were adjusted to zero at 650 nm.



**Fig. 7** (a) Photographs of **NDITA** solids under UV light (365 nm); (i) Amorphous solid, (ii) as-formed **NDITA-1**(TCB), (iii) TMB-immersed HOF, (iv) DMB-immersed HOF and (v) PhCN-immersed HOF. Scale bar: 50 μm. (b) Normalized solid-state fluorescence spectra of amorphous solid (black), as-formed **NDITA-1**(TCB) (green), TMB-immersed HOF (yellow), DMB-immersed HOF (grey), and PhCN-immersed HOF (red).

noted that DMB-immersed HOF showed a new peak at  $2\theta \sim 6^\circ$  (the  $d$  space of 14.9), which was not observed in the pattern of **NDITA-1**(TCB). This indicates that the CT interaction between the DMB and NDI slightly perturbed the structure or periodicity of the framework.

To investigate the conductivity of the HOF, bulk **NDITA-1** crystals that include solvent molecules (TCB, TMB, DMB, and PhCN) in the pores were subjected to flash-photolysis time-



**Fig. 8** Comparison of conductivity transients observed for the bulk crystals of **NDITA-1** immersed in TCB (green), TMB (yellow), DMB (grey) and PhCN (red) upon excitation of 355 nm laser pulses at  $9.1 \times 10^{15} \text{ photons cm}^{-2}$ .

**Table 1.** Photocconductivity of bulk crystals of HOF **NDITA-1** immersed in DMB, TCB, TMB, and PhCN.

Photoconductivity / $10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$	<b>NDITA-1</b> (DMB)	<b>NDITA-1</b> (TCB)	<b>NDITA-1</b> (TMB)	<b>NDITA-1</b> (PhCN)
	9.8	5.0	3.6	4.6

resolved microwave conductivity (FP-TRMC) measurements<sup>51,52</sup> with excitation at 355 nm (Fig. 8). **NDITA-1**(DMB) showed the largest conductivity among them due to effective charge separation: the  $\phi\sum\mu$  value ( $9.8 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) is four times larger than amorphous solid of **NDITA** (Fig. S16), two times larger than the other HOFs (Table 1). The  $\phi\sum\mu$  values of the related NDI-based materials are summarized in Table S4. The measurement on the  $\text{SF}_6$ -treated sample showed a smaller value, indicating that the charge carrier is an electron (Fig. S17). It is also remarkable that the conductivity transient of PhCN-immersed HOF shows no decay even after 90 μs (Fig. S18), indicating that charge carriers may be accumulated in PhCN.

## Conclusions

In summary, we constructed naphthalenediimide (NDI)-based HOF **NDITA-1** using tetratopic carboxylic acid (**NDITA**) that has a NDI core and two dicarboxy-*m*-terphenyl (*DmT*) moieties in nearly orthogonal conformation. The HOF has a slipped stacking structure of H-bonded 2D porous sheets. In the HOF, half part of the NDI surface participates in the formation of 1D stacked columnar domains that act as the electron conducting pathway, while the other half is exposed inside the void channel. Since aromatic solvents can come into contact with the NDI moieties, the HOF exhibits solvent-responsive photophysical and electronic behaviors. Particularly, the HOF encapsulating electron-rich dimethoxybenzene (DMB) in the void enhances charge-transfer interactions, resulting in significant changes in color from pale yellow to brown and quenching of the emission. Furthermore, TRMC measurements on the solvent-immersed HOFs revealed that the DMB-immersed HOF showed the highest electron conductivity among solvent-immersed HOFs in



the present systems. These results indicate that the HOF with  $\pi$ -conjugated moieties partly exposed to the channel surface and partly stacked with neighboring  $\pi$ -conjugated moieties can contribute to the development of materials that enable the dynamic modulation of electronic properties by guest molecules.

## Author contributions

Y. M. synthesized and characterized all materials, evaluated the properties of the materials and co-wrote the paper. R. O. performed the theoretical calculations. R. P. P and S. S. performed conductivity measurements. M. N. and N. T. performed activation of HOFs under critical CO<sub>2</sub> and gas sorption experiments. T. H. and I. H. planned the research and analysed the data. I. H. supervised and co-wrote the paper. All authors discussed the results and commented on the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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## Notes and references

† Crystal data for **NDITA-1**(TCB), C<sub>54</sub>H<sub>30</sub>N<sub>2</sub>O<sub>12</sub>·6(C<sub>6</sub>H<sub>3</sub>Cl<sub>3</sub>); Fw = 1919.4; *triclinic*, *P*-1 (#2), *Z* = 1, *a* = 4.9531(8) Å, *b* = 19.0154(15) Å, *c* = 23.435(2) Å,  $\alpha$  = 112.684(8)°,  $\beta$  = 93.637(11)°,  $\gamma$  = 90.887(10)°, *V* = 2030.5(4) Å<sup>3</sup>, *T* = 100 K, *D* = 1.570 g cm<sup>-3</sup>, 22250 collected, 9320 unique (*R*<sub>int</sub> = 0.2126) reflections, the final *R*<sub>1</sub> and *wR*<sub>2</sub> values 0.1618 [*I* > 2.0 $\sigma$ (*I*)] and 0.4485 (all data), respectively. CCDC-2478400.

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### Data availability

The data supporting this article have been included as part of the ESI.

