

Vertically Expanded Crystalline Porous Covalent Organic Frameworks

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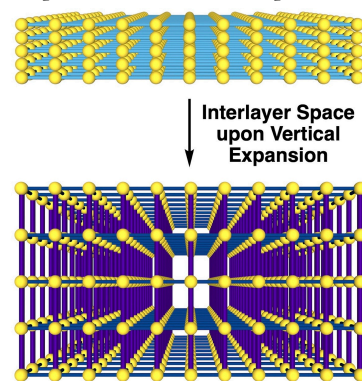
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ABSTRACT: Covalent organic frameworks (COFs) could be developed for molecular confinement and separation. However, their proximate π stacks limit the interlayer distance to be only 3–6 Å, which is too small for guests to enter. As a result, COFs block the access to the x - y space and limit guest entry/exit strictly to only the pores along the z direction. Therefore, the extended faces of each layer are hidden between layers, precluding the possibility of any interactions with guest molecules. Here we report a strategy for opening interlayer spaces of COFs to attain newly accessible nanospace between layers. This becomes possible by using coordination bonds to replace the conventional π - π stacks between layers. We demonstrate this concept by synthesizing two-dimensional covalent cobalt(II) porphyrin layers through topology-guided polymerization, which were piled up by bidentate axial pillars through coordination bonds with cobalt(II) porphyrin along the z direction, assembling vertically expanded COFs via one-pot reaction. The resultant frameworks separate the layers with axial pillars and create discrete apertures between layers defined by the molecular length of pillars. Consequently, the originally inaccessible interlayers are open for guest access, while the polygonal π planes are exposed to trigger various supramolecular interactions. Vapor sorption, breakthrough experiments, and computational studies mutually revealed that the vertically expanded frameworks with optimal interlayer slits induce additional interactions to discriminate benzene and cyclohexane and separate their mixtures efficiently under ambient conditions.



INTRODUCTION

The seven chemical separations exert profound impact on global energy use, carbon emission, and pollution.¹ Among them, benzene (Bz)-cyclohexane (Cy) separation represents the most challenging goal owing to their physical similarity (Table S1).^{2–4} Their boiling points differ by only 0.6 °C (Bz at 353.3 K and Cy at 353.9 K), while the formation of an azeotrope adds more difficulties to separation.⁵ The current technology of extractive distillation and azeotropic distillation involves complex process with energy demand and high cost.^{3,5} It has been a long-lasting target to separate Bz-Cy mixtures in an energy-saving and facile way.^{6–11}

Covalent organic frameworks (COFs) are a class of crystalline porous materials that combine large surface area, tunable pores, and high stability and could be developed for molecular separations. COFs utilize covalent bonds to form extended polygonal backbone (Figure 1A) and develop π - π interactions between layers or interpenetrations for z -directional supramolecular assembly, constituting layered or folded frameworks (Figure 1B).^{12–30} As a result, COFs restrict the guest entry to only one-dimensional (1D) channels along the z direction and prohibit the access to the interlayer x - y space, greatly impeding the full design of skeletons and pores for structural development and functional exploration.^{31,32}

Herein, we report the chemistry to open the interlayer x - y space by inserting molecular pillars as a spacer between 2D layers to create

vertically expanded COFs. We show this strategy by replacing π - π interactions between layers with coordination bonds to open the interlayer space with molecular pillars. We developed a three-component one-pot polymerization system with cobalt(II) porphyrin as knot, phenyl as linker, and bidentate ligands as pillar to construct vertically expanded COFs. The vertically expanded skeletons are designed to be covalently linked to form two-dimensional (2D) layers extended over the x - y plane, which are further polymerized along the z direction via axial ligation between cobalt porphyrin and pillars to spatially expand layers by the pillars (Figure 1C). The vertically expanded COFs open new window for guest entry and exit, expose both up/down faces of each layer to guest molecules, offering new sites for host-guest interactions. The resultant materials with optimal interlayer aperture discriminate Bz from Cy via π - π and C-H... π interactions, enabling an efficient separation of Bz-Cy mixtures under ambient conditions. This study unveils the chemistry to design vertically expanded frameworks via supramolecular polymerizations of layers and construct novel COFs with unique interlayer apertures, showing a new type of framework structures for host-guest assembly, separation, and catalysis.

Three-dimensional (3D) COFs are formed by the covalent link of building units into 3D polygonal skeletons where different degrees of interpenetration involve in shaping the extended porous

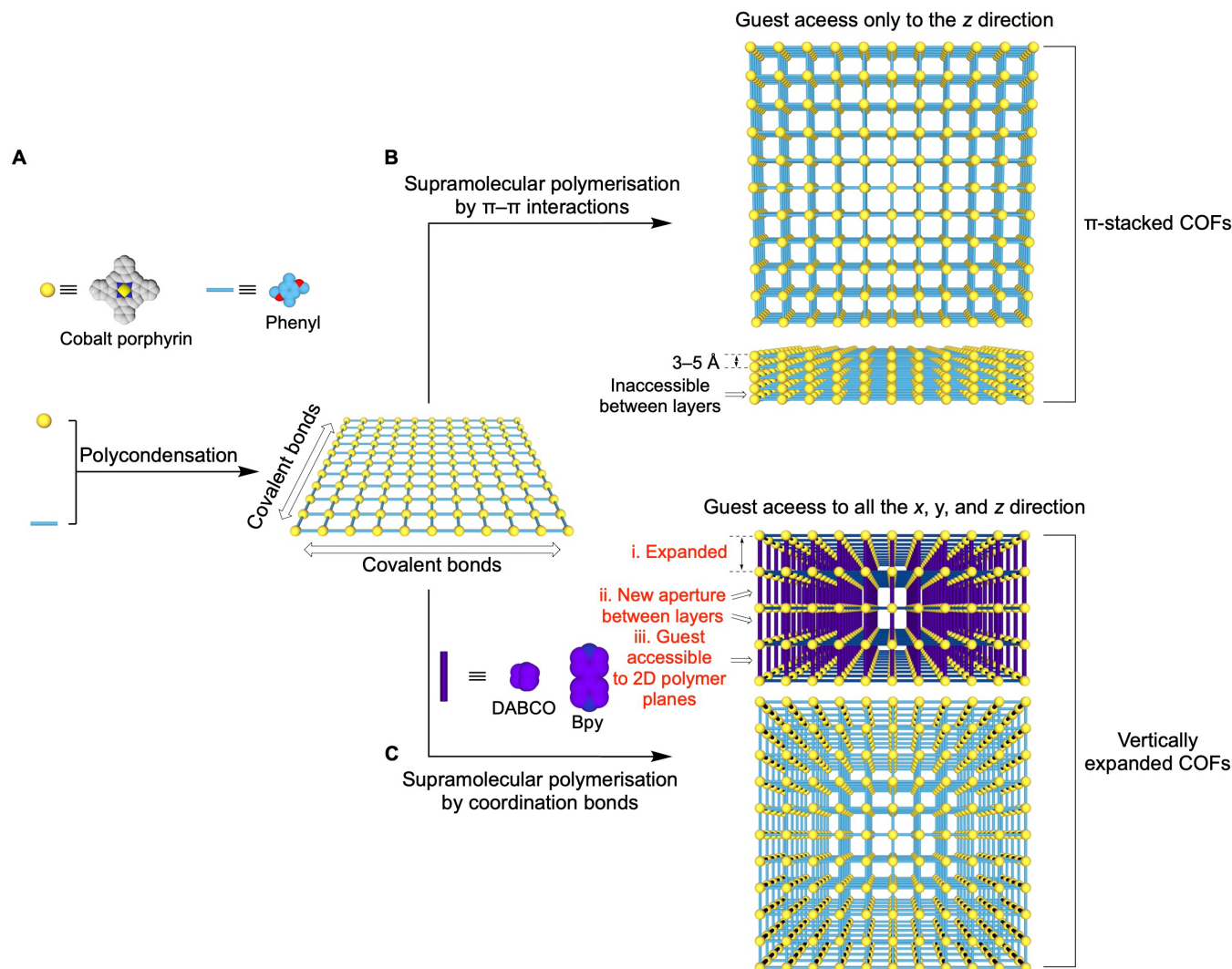


Figure 1. Molecular Design of Vertically Expanded Covalent Organic Frameworks. (A) Polycondensation of knot and linker units to form 2D covalent layer extended over the x - y plane. (B) Simultaneous supramolecular polymerization driven by π - π interactions between layers forms conventional covalent organic frameworks (COFs) with an interlayer distance of 3–6 Å that is too small for guest access (Top panel: Top view; bottom panel: Side view). (C) Introducing interlayer spacer via coordination bonds to guide the supramolecular polymerization of 2D layers along the z direction to create vertically expanded COFs, featuring (i) the interlayer distance is predesigned and managed by the length of pillars, (ii) interlayer aperture is newly developed, and (iii) interlayer is fully opened so that guests are accessible to both up and down faces of the 2D planes (Top panel: Top view; bottom panel: Side view) (five layers are shown; yellow ball: cobalt(II) porphyrin; sky blue stick: phenyl linker; purple stick: interlayer spacer with bidentate ligand, such as DABCO and Bpy).

structures.^{33–42} In sharp contrast, the vertically expanded COFs feature covalently linked 2D polymeric layers, which are polymerized to pile up by inserting axial ligands between layers. Thus, the fundamental structure of vertically expanded COFs remains 2D polygonal layers, while creating new nanospace between layers. The conceptual difference between our strategy and Hofmann clathrates^{43–45} or metal-organic frameworks (MOFs)^{46–48} is that our systems consist of covalently linked polygonal skeletons. Thus, our systems involve both polycondensation and supramolecular polymerization, while Hofmann clathrates or MOFs are only supramolecular polymerization.

RESULTS

Design, Synthesis, and Characterization. We deployed cobalt(II) porphyrin (CoTPP) as a knot and 2,5-dimethoxyterephthaldehyde (DMTA) as a linker, and 1,4-diazabicyclo[2.2.2]octane (DABCO) and 4,4'-dipyridyl (Bpy) as z -

directional bidentate pillars, for the simultaneous Schiff-base polycondensation and supramolecular coordination polymerization in a one-pot reaction system (Figure 2A–C). DABCO and Bpy with nitrogen lone pairs are well-known bidentate ligands to coordinate with cobalt porphyrin via axial ligation to form supramolecular polymers (DABCO→CoTPP and Bpy→CoTPP).^{49,50} One-pot reaction of a mixture of CoTAPP and DABCO or Bpy with DMTA under solvothermal conditions yields crystalline porous DABCO→CoTPP-DMTP-COF and Bpy→CoTPP-DMTP-COF in 81% and 79% yield, respectively. As a control, 2D COF analogue, namely CoTPP-DMTP-COF with π - π stacking layers, was prepared by condensing CoTAPP with DMTA under solvothermal conditions in 83% yield (Figure 2A). DABCO→CoTPP-DMTP-COF and Bpy→CoTPP-DMTP-COF consist of imine-linked 2D layers extended over the x - y plane and vertically expanded skeletons with DABCO and Bpy pillars along the z direction (Figure 2B–2D).

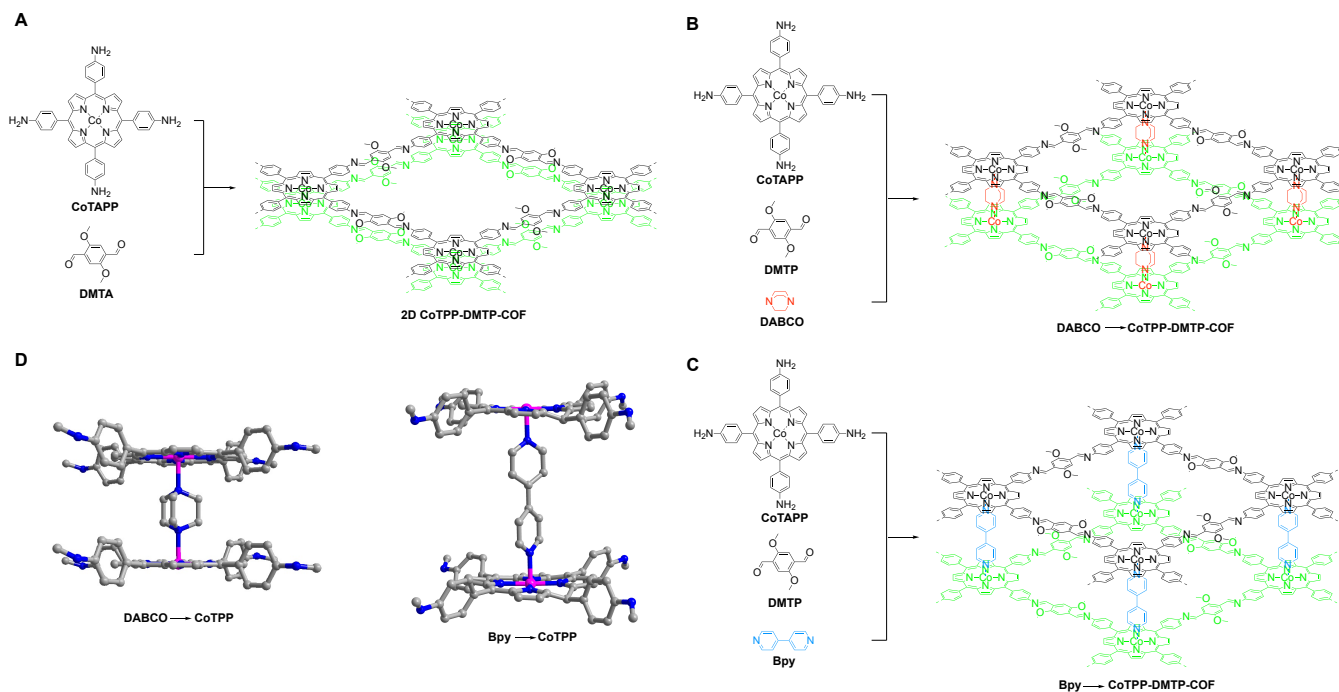


Figure 2. Design and Synthesis. (A) Schematic representation of 2D CoTPP-DMTP-COF with π - π interactions (only two layer and one pore are shown for clarity). (B) Schematic representation of DABCO→CoTPP-DMTP-COF with the coordination bonds between DABCO and cobalt(II) porphyrin along the z axis. (C) Schematic representation of Bpy→CoTPP-DMTP-COF with the coordination bonds between Bpy and cobalt(II) porphyrin along the z axis. (D) Vertically coordinated cobalt porphyrin units by DABCO (left) and BPy (right).

DABCO→CoTPP-DMTP-COF and Bpy→CoTPP-DMTP-COF were characterized by various analytical methods. Fourier transform infrared (FT IR) spectra revealed a strong stretching signal at 1623 cm^{-1} , which was assigned to the imine $\text{C}=\text{N}$ linkages (Figure S1A). For Co-N vibrations, the DABCO→CoTPP-DMTP-COF exhibited vibration bands at 541 and 569 cm^{-1} , whereas the Bpy→CoTPP-DMTP-COF showed bands at 542 and 569 cm^{-1} . In comparison, CoTPP-DMTP-COF displayed bands at 538 and 568 cm^{-1} (Figure S1B). These shifts to longer wavenumbers suggest the occurrence of axial coordination with DABCO and Bpy. Elemental analysis and inductively coupled plasma atomic emission spectroscopy (ICP-AES) confirmed that the C, N, O, and Co contents are consistent with the structures of DABCO→CoTPP-DMTP-COF and Bpy→CoTPP-DMTP-COF (Table S2).

DABCO→CoTPP-DMTP-COF (Figure 3A, black curve) exhibited a powder X-ray diffraction (PXRD) profile with strong peaks at 3.62° , 7.03° , and 10.51° , corresponding to the (100), (200), and (030) facets, respectively, which is distinct from that of CoTPP-DMTP-COF (Figure S2). Structural simulations (Figure 3A, sky blue curve) with non-interpenetrated mode followed by Pawley refinements (Figure 3A, purple cross) yielded a P_1 space group with unit cell parameters of $a = 25.63\text{ \AA}$, $b = 25.64\text{ \AA}$, $c = 6.87\text{ \AA}$, $\alpha = 85.93^\circ$, $\beta = 85.46^\circ$, and $\gamma = 87.34^\circ$ (residues $R_{\text{wp}} = 3.44\%$ and $R_p = 2.70\%$) (Table S3 and see atomistic coordinates in cif). In contrast, simulations with interpenetration structures such as a two-fold model did not pair with the experimentally observed data (Figure S3). Bpy→CoTPP-DMTP-COF displayed PXRD peaks at 3.58° , 4.64° , 7.13° , and 10.77° , which were assigned to the (100), (110), (200), and (310) facets, respectively (Figure 3D, black curve). Pawley refinements (Figure 3D, purple cross) revealed a P_1 space group with unit-cell parameters of $a = 25.64$

$\text{\AA}$, $b = 25.65\text{ \AA}$, $c = 11.10\text{ \AA}$, $\alpha = 93.73^\circ$, $\beta = 85.47^\circ$, and $\gamma = 90.17^\circ$ (residues $R_{\text{wp}} = 1.96\%$ and $R_p = 1.54\%$) (Table S3 and see atomistic coordinates in cif). In this case, multi-fold interpenetration cannot fit the experimental results (Figure S4). Thus, both DABCO→CoTPP-DMTP-COF (Figure 3A, sky blue curve) and Bpy→CoTPP-DMTP-COF (Figure 3D, sky blue curve) consist of a non-interpenetrated vertically expanded structure.

Both DABCO→CoTPP-DMTP-COF (Figure 3B and C) and Bpy→CoTPP-DMTP-COF (Figure 3E and F) retain 2D covalent porphyrin layers, which are spatially connected by DABCO and Bpy pillars to open apertures along the z direction, thus casting a sharp contrast to CoTPP-DMTP-COF with dense π - π stacks. Therefore, the lateral development of polygonal skeletons over the x - y plane is based on covalent imine bonds and driven by Schiff-base polycondensation, while the vertical growth along the z direction is directed by coordination bonds. Consequently, the introduction of coordination bonds for the supramolecular polymerization enables vertical propagation of 2D porphyrin layers and controls their interlayer distance by the length of axial DABCO and Bpy pillars, opening new interlayer nanospace in COFs to allow guest access over the x - y plane.

In CoTPP-DMTP-COF, the interlayer separation is controlled by π - π interactions and it was evaluated to be only $3.81\text{ \AA}$ – a space that is too small to allow guest access to interlayers.^{12,31,32} Therefore, CoTPP-DMTP-COF is accessible only from the z direction. In contrast, DABCO→CoTPP-DMTP-COF and Bpy→CoTPP-DMTP-COF become accessible along all the x , y , and z directions as their interlayer separations are expanded to 6.87 and $11.10\text{ \AA}$, respectively. With these new porous channels between layers, both up and down faces of each 2D porphyrin layer are exposed for supramolecular interactions with guest molecules. Thus, DABCO→CoTPP-DMTP-COF and

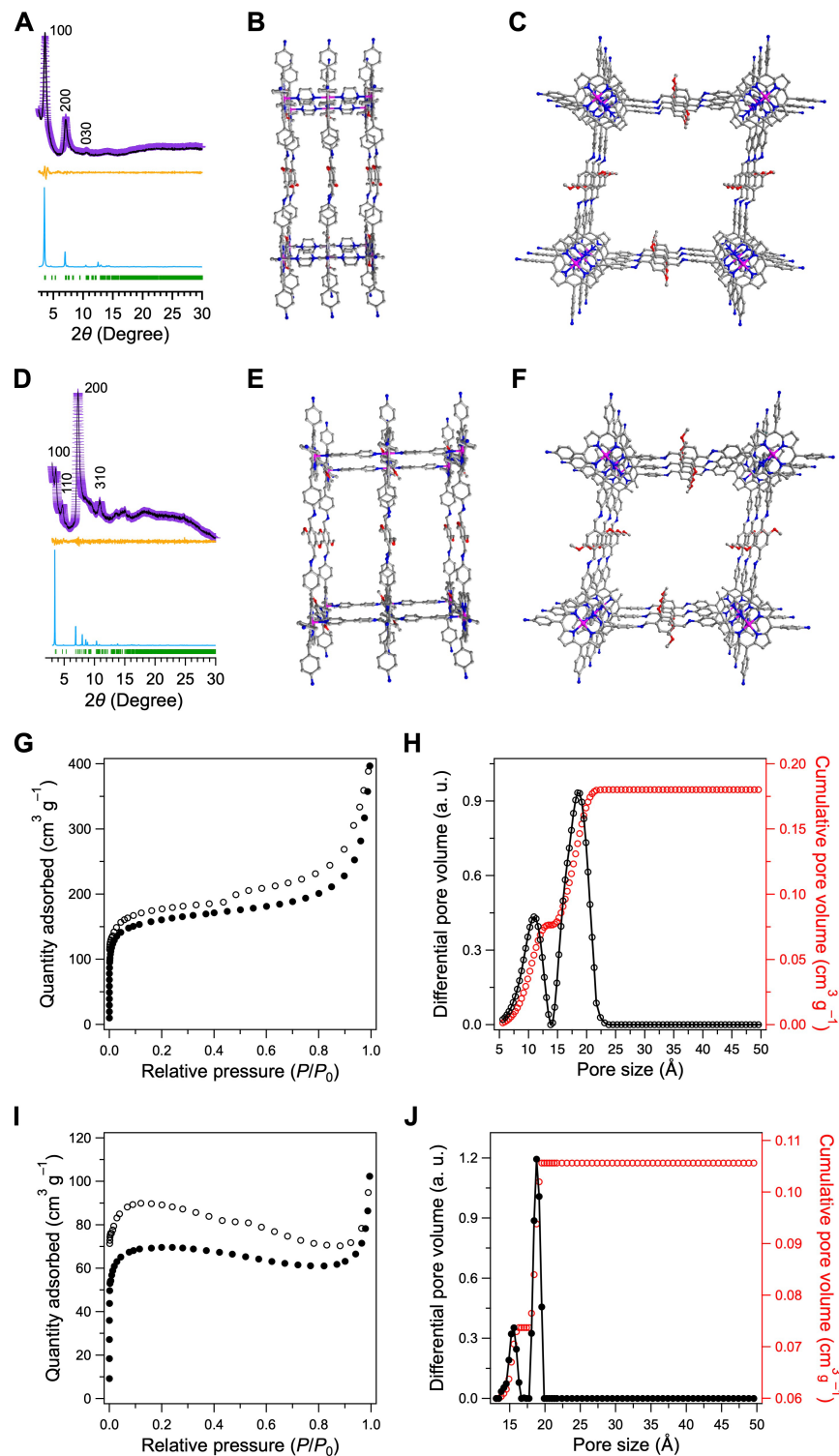


Figure 3. Structure and Characterization. (A) PXRD patterns of DABCO→CoTPP-DMTP-COF of observed (black curve), Pawley refined (purple cross) and their difference (orange curve), the non-interpenetrated mode of the *P1* space group (sky blue curve), and Bragg position (green lines). (B) Side view of reconstructed structure of DABCO→CoTPP-DMTP-COF (Pink: Co; grey: C; blue: N; red: O; H atoms are omitted for clarity). (C) Top view of reconstructed structure of DABCO→CoTPP-DMTP-COF. (D) PXRD patterns of Bpy→CoTPP-DMTP-COF of observed (black curve), Pawley refined (purple cross) and their difference (orange curve), the non-interpenetrated mode of the *P1* space group (sky blue curve), and Bragg position (green lines). (E) Side view of reconstructed structure of Bpy→CoTPP-DMTP-COF. (F) Top view of reconstructed structure of Bpy→CoTPP-DMTP-COF. (G) Nitrogen sorption isotherm of DABCO→CoTPP-DMTP-COF. (H) Pore size distribution (black dots and curve) and pore volume (red dots and curve) of DABCO→CoTPP-DMTP-COF. (I) Nitrogen sorption isotherm of Bpy→CoTPP-DMTP-COF. (J) Pore size distribution (black dots and curve) and pore volume (red dots and curve) of Bpy→CoTPP-DMTP-COF.

Bpy→CoTPP-DMTP-COF create new nanospace between layers for new host-guest chemistry and supramolecular interactions. Distinct from conventional three-dimensional (3D) COFs where layers are folded, the interlayer structures of DABCO→CoTPP-DMTP-COF and Bpy→CoTPP-DMTP-COF are controllable by the axial pillars, rendering the newly developed COFs able to predesign both skeletons and pores.

DABCO→CoTPP-DMTP-COF (Figure 3G) and Bpy→CoTPP-DMTP-COF (Figure 3I) exhibited a rapid uptake of nitrogen at $P/P_0 < 0.1$, suggesting the presence of micropores. DABCO→CoTPP-DMTP-COF and Bpy→CoTPP-DMTP-COF displayed Brunauer–Emmett–Teller (BET) surface areas of 517.1 and 215.3 m² g⁻¹, and a pair of pores of [10.8 and 19 Å] (Figure 3H) and [15.7 and 19 Å] (Figure 3J), respectively. In contrast, CoTPP-DMTP-COF (Figure S5 and S6) exhibited only one type of pores with a size of 19 Å, corresponding to the 1D tetragonal channels. Thus, DABCO→CoTPP-DMTP-COF and Bpy→CoTPP-DMTP-COF form new apertures of 10.8 and 15.7 Å between layers.

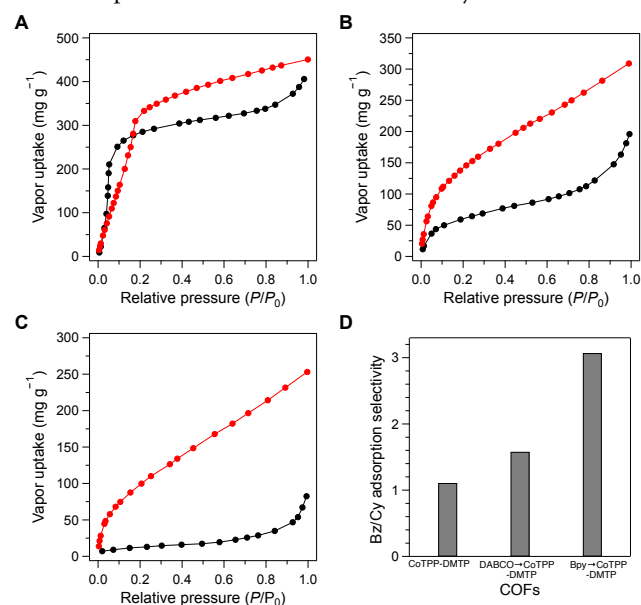


Figure 4. Bz and Cy Adsorption Isotherms. (A–C). Vapor sorption isotherms of Bz (red curve) and Cy (black curve) for (A) CoTPP-DMTP-COF, (B) DABCO→CoTPP-DMTP-COF, and (C) Bpy→CoTPP-DMTP-COF. (D) The Bz/Cy adsorption selectivity for CoTPP-DMTP-COF, DABCO→CoTPP-DMTP-COF, and Bpy→CoTPP-DMTP-COF.

Field emission scanning electron microscopy (FE SEM) of CoTPP-DMTP-COF revealed a spherical morphology (Figure S7), while DABCO→CoTPP-DMTP-COF (Figure S8) and Bpy→CoTPP-DMTP-COF (Figure S9) exhibited thin flake and cubic shapes, respectively. High-resolution transmission electron microscopy (HR TEM, Figure S10–S12) revealed oriented lattice fringes with a domain size of approximately 200 nm, indicating their high structural integrity. Fast-Fourier transform (FFT) revealed pore size of 1.94 nm for CoTPP-DMTP-COF (Figure S10), 1.9 and 0.67 nm for DABCO→CoTPP-DMTP-COF (Figure S11) and 1.89 and 1.55 nm for Bpy→CoTPP-DMTP-COF (Figure S12).

X-ray photoelectron spectroscopy (XPS) revealed that CoTPP-DMTP-COF exhibited two peaks at 398.9 and 398.3 eV (Figure S13A), which were assigned to the pyrrolic N–Co (red curve, 76.3%)

and the imine N=C (blue curve, 23.7%), respectively. In contrast, DABCO→CoTPP-DMTP-COF displayed three peaks at 398.1, 398.6, and 400.6 eV (Figure S13B), corresponding to the imine N=C (purple curve, 15.1%), pyrrolic N–Co (red curve, 67.8%), and axial DABCO N–Co (blue curve, 17.1%), respectively. Similarly, Bpy→CoTPP-DMTP-COF exhibited peaks at 398.5, 399.6, and 400.1 eV (Figure S13C), which were assigned to the imine N=C (purple curve, 20.1%), pyrrolic N–Co (red curve, 47.6%), and axial Bpy N–Co (blue curve, 32.3%), respectively.⁵¹ The Co 2p spectroscopy of CoTPP-DMTP-COF revealed two peaks (2p_{1/2} and 2p_{3/2}), at 795.4 and 779.8 eV, confirming the cobalt coordination within the porphyrin macrocycle. The 2p_{1/2} and 2p_{3/2} peaks shift to 795.0 and 779.6 eV for DABCO→CoTPP-DMTP-COF and 795.1 and 779.7 eV for Bpy→CoTPP-DMTP-COF (Figure S14). DABCO induces a relatively larger shift, indicating a stronger coordination. These shifts confirmed successful coordination between cobalt and the axial ligands.

Benzene (Bz) and Cyclohexane (Cy) Adsorption. Owing to the vertical interlayer pores presented by DABCO→CoTPP-DMTP-COF and Bpy→CoTPP-DMTP-COF, we explored these newly opened nanospace for the molecular separation of Bz and Cy. Vapor adsorption isotherm experiments at 298 K revealed that DABCO→CoTPP-DMTP-COF and Bpy→CoTPP-DMTP-COF exhibited different absorption features from CoTPP-DMTP-COF. CoTPP-DMTP-COF displayed sharp absorptions for both Bz and Cy with a higher absorption capacity for Cy than Bz (Figure 4A) at low pressure region $P/P_0 < 0.12$. The isotherm curves revealed a cross point at $P/P_0 = 0.17$, after which CoTPP-DMTP-COF exhibited a higher uptake of Bz than Cy. As a result, CoTPP-DMTP-COF displayed a low Bz/Cy adsorption selectivity of 1.1 at $P/P_0 = 0.98$. In sharp contrast, both DABCO→CoTPP-DMTP-COF (Figure 4B) and Bpy→CoTPP-DMTP-COF (Figure 4C) exhibited higher Bz adsorption than Cy over the whole P/P_0 range. In the case of DABCO→CoTPP-DMTP-COF, the Bz adsorption increases sharply at low $P/P_0 < 0.1$ and increases linearly to reach a capacity of 309.2 mg g⁻¹ at $P/P_0 = 0.98$ (Fig. 4B, red dots and curve). On contrary, the Cy uptake increases sluggishly to display a capacity of only 196.1 mg g⁻¹ (Figure 4B, black dots and curve). More explicitly, in the case of Bpy→CoTPP-DMTP-COF, the Cy adsorption is much far sluggish over a wide P/P_0 range to show a capacity of only 82.5 mg g⁻¹ (Figure 4C, black dots and curve), while the Bz adsorption increased sharply to reach a capacity of 253.2 mg g⁻¹ (Figure 4C, red dots and curve). Thus, the Bz/Cy selectivity is increased to 1.6 and 3.1 for DABCO→CoTPP-DMTP-COF and Bpy→CoTPP-DMTP-COF, respectively (Figure 4D). These results revealed that the vertically expanded COFs drastically change their Bz and Cy adsorption behaviors and greatly increased Bz/Cy adsorption selectivity.

Notably, the Bz/Cy adsorption selectivity of Bpy→CoTPP-DMTP-COF is much superior to those of previously reported COFs including COF-300-rt (1.38),⁵² COF-300-st (1.61),⁵² LZU-111 (1.26),⁵² COF-1 (2.45),⁵³ JUC-641 (1.93),⁵⁴ and JUC-642 (2.02)⁵⁴ and exceeds the those of porous organic polymers (POPs) such as CCTF-3,⁵⁵ MALP-1,⁵⁶ PAN-2,⁵⁷ CMP-S-1,⁵⁸ and POP-1,⁵⁹ and metal-organic frameworks (MOFs) such as CUB-5,⁶⁰ MOF-5,⁶⁰ NENU-29,⁶¹ Cu₃(BTC)₂,⁶¹ Co(pybz)₂,⁶² and Cu(bpp)₂(BF₄)₂⁶³ (Table S4).

We carried out ideal adsorbed solution theory (IAST)⁶⁴ calculations to show the adsorption selectivity of Bz/Cy in these three COFs. The isotherms of both Bz and Cy were fitted with dual-site Langmuir Freundlich (DSLFF) model (Tables S5). Bpy→CoTPP-DMTP-COF

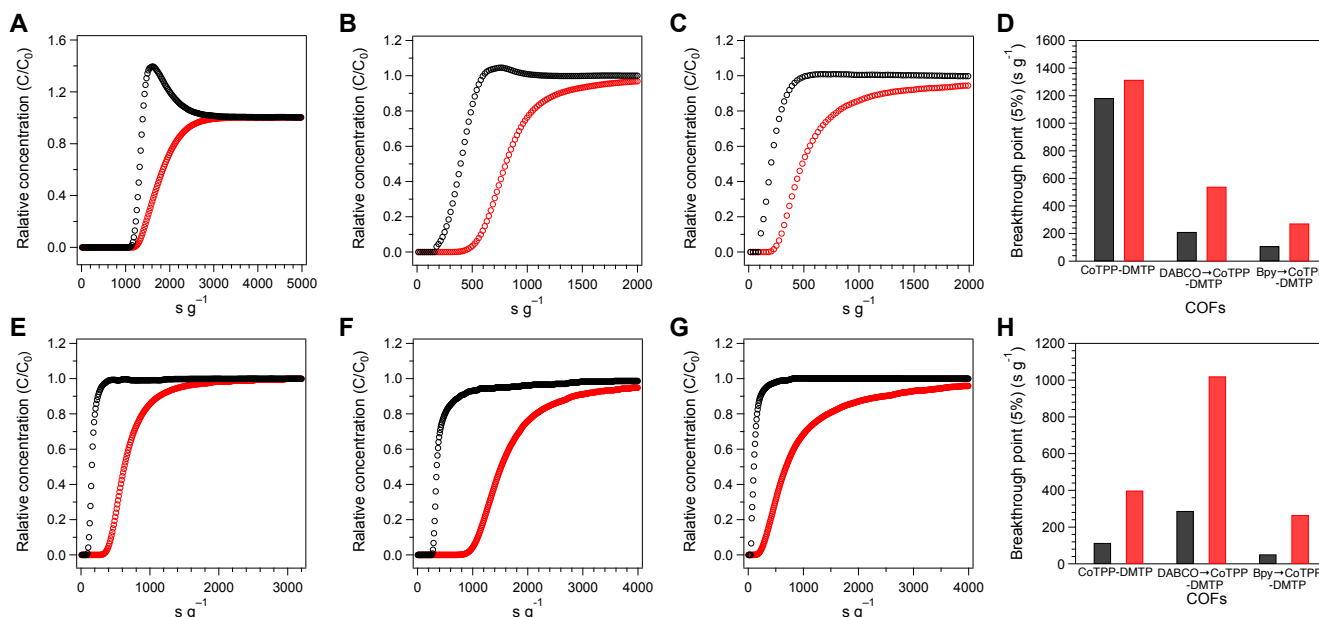


Figure 5. Breakthrough Profiles. (A–C) Breakthrough curves of (A) CoTPP-DMTP-COF, (B) DABCO→CoTPP-DMTP-COF, and (C) Bpy→CoTPP-DMTP-COF for a Cy/Bz mixture (50/50 in vol.) at 298 K and 1 bar (black dots for Cy and red dots for Bz). (D) Comparison of breakthrough points of Cy (black bars) and Bz (red bars). (E–G) Breakthrough curves of (E) CoTPP-DMTP-COF, (F) DABCO→CoTPP-DMTP-COF, and (G) Bpy→CoTPP-DMTP-COF for a Cy/Bz mixture (95/5 in vol.) at 298 K and 1 bar (black dots for Cy and red dots for Bz). (H) Comparison of breakthrough points of Cy (black bars) and Bz (red bars).

(red dots) shows a high selectivity (60) at low pressure, which decreases as pressure rises (Figure S15). For the Bz/Cy (50/50) mixture, selectivity stabilizes around 10 kPa, while for the Bz/Cy (5/95) mixture, it shows peak at 4 kPa before dropping, indicating strong competition at intermediate pressures. DABCO→CoTPP-DMTP-COF (blue dots) maintains better selectivity than CoTPP-DMTP-COF (black dots), confirming superior separation performance.

Breakthrough Separations. We carried out direct separation through breakthrough experiments at 298 K at 1 bar by passing Cy/Bz mixtures at a volume ratio of 50/50 or 95/5 through the COF columns (Figure 5, Tables S6–S8, and Tables S12–S14). For a Cy/Bz mixture of 50/50 (vol.), CoTPP-DMTP-COF (Figure 5A and Table S6) exhibited that the Cy component (black dots) passes through the column first with a breakthrough point at 1183.9 s g^{-1} (Figure 5D), while the Bz component (red dots) shows a breakthrough point at 1316.3 s g^{-1} (Figure 5D). As a result, CoTPP-DMTP-COF did not separate the mixture into pure Cy and Bz components owing to a short separation time (132.4 s g^{-1}). In sharp contrast, experiments on DABCO→CoTPP-DMTP-COF (Figure 5B and Table S7) revealed that the Cy component (black dots) passes through the column more shortly with a breakthrough point at 212.6 s g^{-1} (Figure 5D), while the Bz component (red dots) has a breakthrough point at 540.7 s g^{-1} (Figure 5D). Therefore, DABCO→CoTPP-DMTP-COF discriminates Cy and Bz with a long enough breakthrough separation time of 328.1 s g^{-1} , which is much far superior to that (132.4 s g^{-1}) of CoTPP-DMTP-COF. On the other hand, in the case of Bpy→CoTPP-DMTP-COF (Figure 5C and Table S8), the Cy component passes through the column even more quickly to show a breakthrough point at only 109.5 s g^{-1} (Figure 5D). However, in this case, the Bz component reaches a breakthrough point at 274.1 s g^{-1} (Figure 5D). Thus, the breakthrough separation time is 164.6 s g^{-1} , which is larger than that of CoTPP-DMTP-COF but smaller than that

of DABCO→CoTPP-DMTP-COF (Figure 5D). Therefore, the separation of Cy/Bz mixture (50/50 vol.) follows an order of DABCO→CoTPP-DMTP-COF > Bpy→CoTPP-DMTP-COF > CoTPP-DMTP-COF. Among the series, the DABCO→CoTPP-DMTP-COF column offer pure Cy component before the breakthrough point of the Bz component.

Significantly, repeating breakthrough experiments with a Cy/Bz mixture (50/50 in vol.) at 298 K and 1 bar revealed that the separation performance is consistent with the result of the initial breakthrough experiment, conforming the reliability and reproducibility of COFs in separation of Cy/Bz mixture (Figure S16 and Table S9–S11). The PXRD patterns did not shown significant shifts in peak positions or changes in intensity (Figure S17), the absorption spectra remained unchanged (Figure S18), and the COFs retained their original morphology (Figure S19), confirming structural integrity and stability before and after the reaction.

For real implementation, the separation of the Cy/Bz mixture with a low content of Bz at a volume ratio of 95/5 is more profound. The breakthrough point of the Cy component is 114.5 s g^{-1} for CoTPP-DMTP-COF (Figure 5E, black dots and Table S12), 288.4 s g^{-1} for DABCO→CoTPP-DMTP-COF (Figure 5F, black dots and Table S13), and 52.1 s g^{-1} for Bpy→CoTPP-DMTP-COF (Figure 5G, black dots and Table S14), while the breakthrough point of the Bz component is increased to 399.8, 1021.2, and 266.8 s g^{-1} for CoTPP-DMTP-COF (Figure 5E, red dots and Table S12), DABCO→CoTPP-DMTP-COF (Figure 5F, red dots and Table S13), and Bpy→CoTPP-DMTP-COF (Figure 5G, red dots and Table S14), respectively. Thus, the difference in the breakthrough points of the Cy and Bz components is 285.3, 732.8, and 214.7 s g^{-1} for CoTPP-DMTP-COF, DABCO→CoTPP-DMTP-COF, and Bpy→CoTPP-DMTP-COF, respectively (Figure 5H). Remarkably, before the breakthrough point of Bz, the Cy component was separated by the

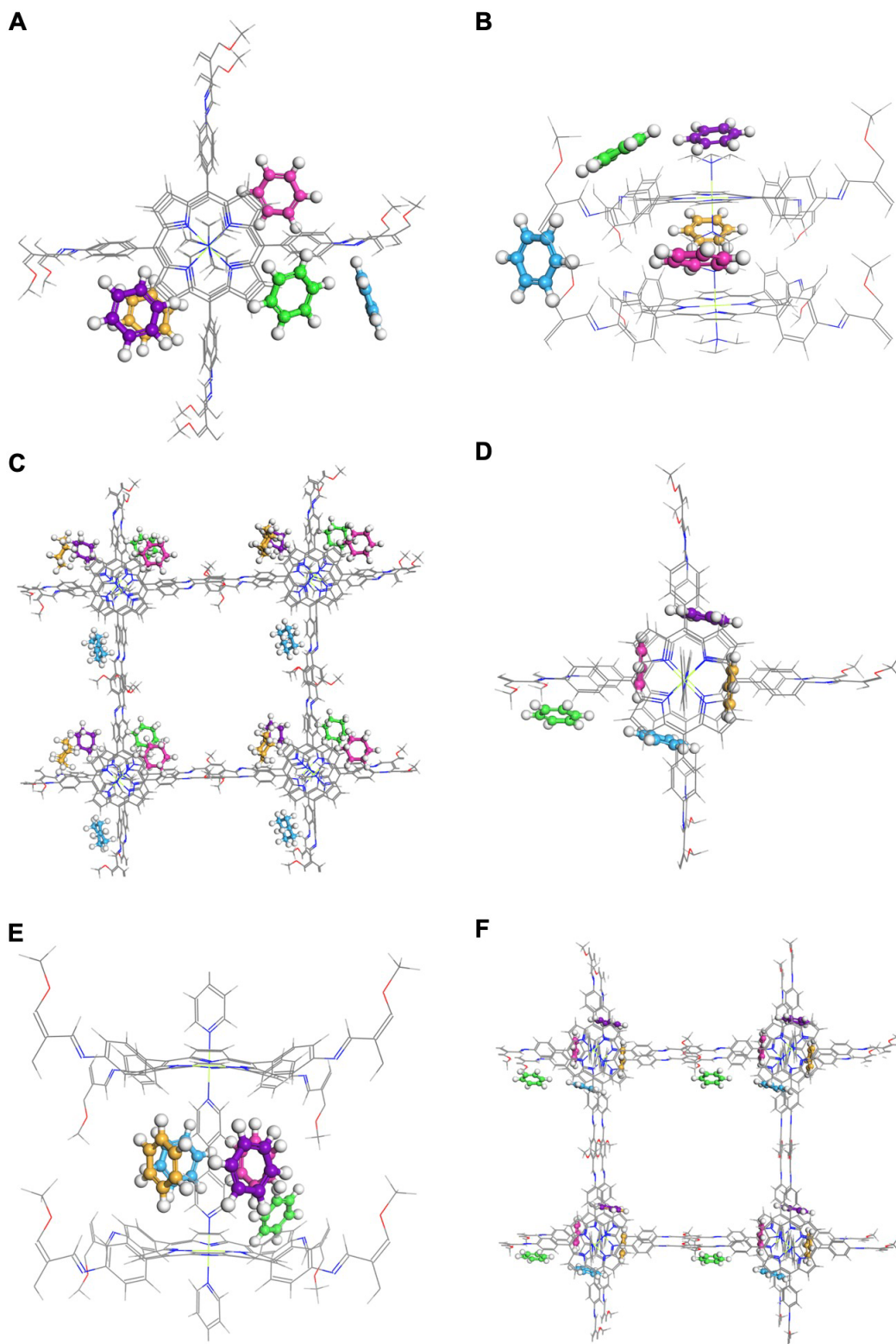


Figure 6. Host-Guest Assembly between COFs and Benzene. (A–C) Molecular interactions between DABCO→CoTPP-DMTP-COF and Bz molecules in the unit cell of (A) top view, (B) side view, and (C) extended two-layer structure. (D–F) Molecular interactions between Bpy→CoTPP-DMTP-COF and Bz molecules in the unit cell of (D) top view, (E) side view, and (F) extended two-layer structure.

DABCO→CoTPP-DMTP-COF column. These results disclose that DABCO→CoTPP-DMTP-COF allows quick separation of Cy from Bz to produce pure Cy and Bz components under ambient conditions.

Although the Bz/Cy selectivity of DABCO→CoTPP-DMTP-COF is lower than that of Bpy→CoTPP-DMTP-COF, its higher adsorption capacities and diffusion coefficients for both Bz and Cy (Figure S20

and Tables S15 and S16) result in superior separation performance for breakthrough experiments with Bz/Cy mixtures of 50/50 and 5/95 (v/v).

DISCUSSION

We utilized density of function tight binding (DFTB) methods to investigate interactions between COFs and Cy or Bz based on a supercell structure ($1 \times 1 \times 2$) and five Cy and Bz molecules.^{65–67} The interaction types and their corresponding distances were summarized in Tables S17–S22, indicating the importance of new interlayer nanospace for the selective confinement and separation of Bz/Cy mixture. For CoTPP-DMTP-COF, the five Cy molecules interact with C–H units of aromatic walls via van der Waals forces, as well as hydrogen bonding interactions with the nitrogen atom of the C=N linkage and the oxygen atom of the methoxy unit (Figure S21A), which gain an average binding energy of $-43.0 \text{ kJ mol}^{-1}$ (Table S23). On the other hand, the interactions between Bz and pore walls are dominated by C–H $\cdots\pi$ interactions and hydrogen-bonding interactions with the nitrogen atom of the C=N linkage and the oxygen atom of the methoxy unit (Figure S21B), leading to an average binding energy of $-47.4 \text{ kJ mol}^{-1}$ (Table S24). These interactions are limited to the 1D channels.

In vertically expanded COFs, the up and down faces of 2D layers as well as the pillars are exposed to Cy and Bz, triggering new host-guest interactions. For DABCO $\rightarrow$ CoTPP-DMTP-COF, two Cy molecules are located at DABCO by C–H $\cdots\pi$ interactions, two Cy molecules are confined on the top of porphyrin unit by C–H $\cdots\pi$ interactions, while one Cy molecule is located at the C=N linkage via hydrogen-bonding interactions (Figure S22A–C). These interactions lead to an average binding energy of $-45.7 \text{ kJ mol}^{-1}$ (Table S25). On the other hand, two Bz molecules are located at DABCO pillar via π – π interactions, two Bz molecules are confined on the up face of porphyrin unit by π – π interaction, while one Bz molecule is located at the C=N linkage through hydrogen-bonding interactions (Figure 6A–C). These interactions gain an average binding energy of $-49.4 \text{ kJ mol}^{-1}$ (Table S26).

Regarding Bpy $\rightarrow$ CoTPP-DMTP-COF, two Cy molecules are located at Bpy via C–H $\cdots\pi$ interactions, two Cy molecules are positioned on the up face of phenyl units of the porphyrin knot by C–H $\cdots\pi$ interactions, while one Cy molecule is located at the C=N linkage via hydrogen-bonding interactions (Figure S22D–F). These interactions lead to an average binding energy of $-37.5 \text{ kJ mol}^{-1}$ (Table S27). On the other hand, four Bz molecules are located at Bpy via π – π and C–H $\cdots\pi$ interactions, while one Bz molecule is positioned at the C=N linkage by hydrogen-bonding interaction (Figure 6D–F). These interactions attain an average binding energy of $-38.1 \text{ kJ mol}^{-1}$ (Table S28).

These comparative studies revealed that DABCO $\rightarrow$ CoTPP-DMTP-COF triggers much stronger interactions with Bz compared to Cy, among these COFs. The distinct gap in the binding energy between Bz and Cy endows DABCO $\rightarrow$ CoTPP-DMTP-COF with high selectivity, leading to the separation of the Cy/Bz mixtures to produce pure Cy and Bz components under ambient conditions. The vertically expanded COFs present newly opened pores between 2D layers that offer unique nanospace to trigger supramolecular interactions and facilitate molecular adsorption and separation.

CONCLUSIONS

In summary, we have reported a novel class of COFs by introducing predesigned molecular spacer between 2D layers to construct vertically

expanded frameworks. A distinct feature is that the supramolecular polymerization of the 2D layers is molecularly programmable and controlled by the axial pillars, constituting COFs with vertically expanded yet controlled interlayer apertures. This newly generated interlayer pores are distinct from those of conventional 2D and 3D COFs, where interlayer and folding structures hardly produce pores. Dramatically, the vertically expanded COFs offer new nanospace for host-guest interactions and open new windows between layers to allow for the guest access from all the *x*, *y* and *z* directions, paving a way to fully use of COF skeleton and porous structures. These structures highlight new binding sites at the 2D layers and increase benzene uptake with newly developed π – π and C–H $\cdots\pi$ interactions, rendering the system able to separate Cy/Bz mixtures to produce pure components under ambient conditions. Our strategy creates a family of novel COFs which are distinct from conventionally obtained frameworks and offers a platform for designing open framework materials to develop host-guest assembly, separation, catalysis, and energy storage.

ASSOCIATED CONTENT

Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>. General material; Methods and characterizations; COFs synthesis procedures; FT IR spectra; PXRD patterns; N₂ adsorption; FE SEM images; HR TEM images; XPS spectra; Molecular interactions calculation; Supporting Figures, Supporting Tables; and Supporting Reference.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Sholl, D. S.; Lively, R. P. Seven Chemical Separations to Change the World. *Nature* **2016**, *532*, 435–437.
- (2) Mukherjee, S.; Sensharma, D.; Qazvini, O. T.; Dutta, S.; Macreadie, L. K.; Ghosh, S. K.; Babarao, R. Advances in Adsorptive Separation of Benzene and Cyclohexane by Metal-Organic Framework Adsorbents. *Coord. Chem. Rev.* **2021**, *437*, 213852.
- (3) Villaluenga, J. G.; Tabe-Mohammadi, A. A Review on the Separation of Benzene/Cyclohexane Mixtures by Pervaporation Processes. *J. Membr. Sci.* **2000**, *169*, 159–174.
- (4) Dreisbach, R. R. (Ed.). Physical Properties of Chemical Compounds—III. *Amer. Chem. Soc.* **1961**.
- (5) Speight, J. G. Handbook of Industrial Hydrocarbon Processes. *Gulf Professional Pub.* **2019**.
- (6) Ruthven, D. M. Past Progress and Future Challenges in Adsorption Research. *Ind. Eng. Chem. Res.* **2000**, *39*, 2127–2131.
- (7) Wu, Y.; Weckhuysen, B. M. Separation and Purification of Hydrocarbons with Porous Materials. *Angew. Chem., Int. Ed.* **2021**, *60*, 18930–18949.
- (8) Angelini, P.; Armstrong, T.; Counce, R.; Griffith, W.; LKlasson, T.; Muralidharan, G.; Narula, C.; Sikka, V.; Closset, G.; Keller, G. Materials for Separation Technologies: Energy and Emission Reduction Opportunities. *DOE, EERE Office, Washington, DC*, **2005**.
- (9) Bu, X. H.; Zaworotko, M. J.; Zhang, Z. (Eds.). Metal-Organic Framework: From Design to Applications. *Springer International Publishing*. **2020**.
- (10) Wang, Z.; Zhang, S.; Chen, Y.; Zhang, Z.; Ma, S. Covalent Organic Frameworks for Separation Applications. *Chem. Soc. Rev.* **2020**, *49*, 708–735.
- (11) Yang, L.; Qian, S.; Wang, X.; Cui, X.; Chen, B.; Xing, H. Energy-efficient Separation Alternatives: Metal-Organic Frameworks and Membranes for Hydrocarbon Separation. *Chem. Soc. Rev.* **2020**, *49*, 5359–5406.
- (12) Tan, K.T.; Ghosh, S.; Wang, Z.; Wen, F.; Rodriguez-San-Miguel, D.; Feng, J.; Huang, N.; Wang, W.; Zamora, F.; Feng, X.; Thomas, A.; Jiang, D. Covalent Organic Frameworks. *Nat. Rev. Methods Primers* **2023**, *3*, 1.
- (13) Yu, B.; Lin, R.B.; Xu, G.; Fu, Z.H.; Wu, H.; Zhou, W.; Lu, S.; Li, Q.W.; Jin, Y.; Li, J.H.; Zhang, Z.; Wang, H.; Yan, Z.; Liu, X.; Wang, K.; Chen, B.; Jiang, J. Linkage Conversions in Single-crystalline Covalent Organic Frameworks. *Nat. Chem.* **2024**, *16*, 114–121.
- (14) Liu, R.; Tan, K.T.; Gong, Y.; Chen, Y.; Li, Z.; Xie, S.; He, T.; Lu, Z.; Yang, H.; Jiang, D. Covalent Organic Frameworks: An Ideal Platform for Designing Ordered Materials and Advanced Applications. *Chem. Soc. Rev.* **2021**, *50*, 120–242.
- (15) Zhao, X.; Pachfule, P.; Thomas, A. Covalent Organic Frameworks (COFs) for Electrochemical Applications. *Chem. Soc. Rev.* **2021**, *50*, 6871–6913.
- (16) Yuan, M.; Ma, F.; Chen, L.; Li, B.; Dai, X.; Shu, J.; He, L.; Chen, J.; Lin, S.; Xie, G.; Chai, Z.; Wang, S. Hydrogen Isotope Effect Endows a Breakthrough in Photoluminescent Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2024**, *146*, 1250–1256.
- (17) Galeotti, G.; De Marchi, F.; Hamzehpoor, E.; MacLean, O.; Rajeswara Rao, M.; Chen, Y.; Besteiro, L.V.; Dettmann, D.; Ferrari, L.; Frezza, F.; Sheverdyaeva, P. M.; Liu, R.; Kundu, A. K.; Moras, P.; Ebrahimi, M.; Gallagher, M. C.; Rosei, F.; Perepichka, D. F.; Contini, G. Synthesis of Mesoscale Ordered Two-dimensional π -conjugated Polymers with Semiconducting Properties. *Nat. Mater.* **2020**, *19*, 874–880.
- (18) Li, Z.; Deng, T.; Ma, S.; Zhang, Z.; Wu, G.; Wang, J.; Li, Q.; Xia, H.; Yang, S.W.; Liu, X. Three-component Donor- π -Acceptor Covalent-Organic Frameworks for Boosting Photocatalytic Hydrogen Evolution. *J. Am. Chem. Soc.* **2023**, *145*, 8364–8374.
- (19) Lu, M.; Liu, J.; Li, Q.; Zhang, M.; Liu, M.; Wang, J.L.; Yuan, D.Q.; Lan, Y.Q. Rational Design of Crystalline Covalent Organic Frameworks for Efficient CO₂ Photoreduction With H₂O. *Angew. Chem., Int. Ed.* **2019**, *58*, 12392–12397.
- (20) Li, X.; Wang, H.; Chen, H.; Zheng, Q.; Zhang, Q.; Mao, H.; Liu, Y.; Cai, S.; Sun, B.; Dun, C.; Gordon, M. P.; Zheng, H.; Reimer, J. A.; Urban, J. J.; Ciston, J.; Tan, T.; Chan, E. M.; Zhang, J.; Liu, Y. Dynamic Covalent Synthesis of Crystalline Porous Graphitic Frameworks. *Chem* **2020**, *6*, 933–944.
- (21) Chen, Z.; Wang, J.; Hao, M.; Xie, Y.; Liu, X.; Yang, H.; Waterhouse, G.I.; Wang, X.; Ma, S. Tuning Excited State Electronic Structure and Charge Transport in Covalent Organic Frameworks for Enhanced Photocatalytic Performance. *Nat. Commun.* **2023**, *14*, 1106.
- (22) Xu, H.; Gao, J.; Jiang, D. Stable, Crystalline, Porous, Covalent Organic Frameworks as a Platform for Chiral Organocatalysts. *Nat. Chem.* **2015**, *7*, 905–912.
- (23) Feng, J.; Zhang, Y.J.; Ma, S.H.; Yang, C.; Wang, Z.P.; Ding, S.Y.; Li, Y.; Wang, W. Fused-Ring-Linked Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2022**, *144*, 6594–6603.
- (24) Lukose, B.; Kuc, A.; Heine, T. The Structure of Layered Covalent-Organic Frameworks. *Chem. Eur. J.* **2011**, *17*, 2388–2392.
- (25) Wu, X.; Han, X.; Liu, Y.; Liu, Y.; Cui, Y. Control Interlayer Stacking and Chemical Stability of Two-Dimensional Covalent Organic Frameworks via Steric Tuning. *J. Am. Chem. Soc.* **2018**, *140*, 16124–16133.
- (26) Xu, X.; Wu, X.; Xu, K.; Xu, H.; Chen, H.; Huang, N. Pore Partition in Two-Dimensional Covalent Organic Frameworks. *Nat. Commun.* **2023**, *14*, 3360.
- (27) Chen, D.; Chen, W.; Wu, Y.; Wang, L.; Wu, X.; Xu, H.; Chen, L. Covalent Organic Frameworks Containing Dual O₂ Reduction Centers for Overall Photosynthetic Hydrogen Peroxide Production. *Angew. Chem., Int. Ed.* **2023**, *62*, e202217479.
- (28) Weng, W.; Guo, J. Chiral Covalent Organic Framework Films with Enhanced Photoelectrical Performances. *J. Am. Chem. Soc.* **2024**, *146*, 13201–13209.
- (29) Zhang, J.; Cheng, C.; Guan, L.; Jiang, H. L.; Jin, S. Rapid Synthesis of Covalent Organic Frameworks with a Controlled Morphology: An Emulsion Polymerization Approach via the Phase Transfer Catalysis Mechanism. *J. Am. Chem. Soc.* **2023**, *145*, 21974–21982.
- (30) Han, J.; Feng, J.; Kang, J.; Chen, J.M.; Du, X.Y.; Ding, S.Y.; Liang, L.; Wang, W. Fast Growth of Single-Crystal Covalent Organic Frameworks for Laboratory X-Ray Diffraction. *Science* **2024**, *383*, 1014–1019.
- (31) Li, Z.; He, T.; Gong, Y.; Jiang, D. Covalent Organic Frameworks: Pore Design and Interface Engineering. *Acc. Chem. Res.* **2020**, *53*, 1672–1685.
- (32) Deng, L.; Ding, Z.; Ye, X.; Jiang, D. Covalent Organic Frameworks: Chemistry of Pore Interface and Wall Surface Perturbation and Impact on Functions. *Acc. Mater. Res.* **2022**, *3*, 879–893.
- (33) El-Kaderi, H.M.; Hunt, J.R.; Mendoza-Cortés, J.L.; Côté, A.P.; Taylor, R.E.; O’Keeffe, M.; Yaghi, O.M. Designed Synthesis of 3D Covalent Organic Frameworks. *Science* **2007**, *31*, 268–272.
- (34) Liu, Y.; Diercks, C.S.; Ma, Y.; Lyu, H.; Zhu, C.; Alshimmiri, S.A.; Alshihri, S.; Yaghi, O.M. 3D Covalent Organic Frameworks of Interlocking 1D Square Ribbons. *J. Am. Chem. Soc.* **2018**, *141*, 677–683.
- (35) Gao, C.; Li, J.; Yin, S.; Sun, J.; Wang, C. Twist Building Blocks from Planar to Tetrahedral for the Synthesis of Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2020**, *142*, 3718–3723.
- (36) Zhu, Q.; Wang, X.; Clowes, R.; Cui, P.; Chen, L.; Little, M.A.; Cooper, A.I. 3D Cage COFs: A Dynamic Three-dimensional Covalent Organic Framework with High-connectivity Organic Cage Nodes. *J. Am. Chem. Soc.* **2020**, *142*, pp.16842–16848.
- (37) Li, Z.; Sheng, L.; Wang, H.; Wang, X.; Li, M.; Xu, Y.; Cui, H.; Zhang, H.; Liang, H.; Xu, H.; He, X. Three-dimensional Covalent Organic Framework with ceq Topology. *J. Am. Chem. Soc.* **2020**, *143*, 92–96.
- (38) Li, H.; Chen, F.; Guan, X.; Li, J.; Li, C.; Tang, B.; Valtchev, V.; Yan, Y.; Qiu, S.; Fang, Q. Three-dimensional Triptycene-based Covalent Organic Frameworks with ceq or acs Topology. *J. Am. Chem. Soc.* **2021**, *143*, 2654–2659.
- (39) Bao, R.; Xiang, Z.; Qiao, Z.; Yang, Y.; Zhang, Y.; Cao, D.; Wang, S. Designing Thiophene - enriched Fully Conjugated 3D Covalent Organic

Framework as Metal-free Oxygen Reduction Catalyst for Hydrogen Fuel Cells. *Angew. Chem. Int. Ed.* **2023**, *62*, e202216751.

(40) Liu, Y.; Ma, Y.; Zhao, Y.; Sun, X.; Gándara, F.; Furukawa, H.; Liu, Z.; Zhu, H.; Zhu, C.; Suenaga, K.; Oleynikov, P.; Alshammari, A.S.; Zhang, X.; Terasaki, O.; Yaghi, O.M. Weaving of Organic Threads into A Crystalline Covalent Organic Framework. *Science* **2016**, *351*, 365–369.

(41) Lu, M.; Zhang, S.B.; Li, R.H.; Dong, L.Z.; Yang, M.Y.; Huang, P.; Liu, Y.F.; Li, Z.H.; Zhang, H.; Zhang, M.; Li, S.L. Lan, Y.Q. 3D Covalent Organic Frameworks with 16-Connectivity for Photocatalytic C(sp³)-C(sp²) Cross-Coupling. *J. Am. Chem. Soc.* **2024**, *146*, 25832–25840.

(42) Jadhav, T.; Fang, Y.; Liu, C.H.; Dadvand, A.; Hamzehpoor, E.; Patterson, W.; Jonderian, A.; Stein, R.S.; Perepichka, D.F. Transformation between 2D and 3D Covalent Organic Frameworks via Reversible [2+ 2] Cycloaddition. *J. Am. Chem. Soc.* **2020**, *142*, 8862–8870.

(43) Hasegawa, T.; Nishikiori, S.I.; Iwamoto, T. The Crystal Structures of α,ω -Diaminoalkane-cadmium (II) Tetracyanonickelate (II)-Aromatic Molecule Inclusion Compounds. II. 1,6-Diaminohexane-cadmium (II) Tetracyanonickelate (II)-o-toluidine (1/1): $\text{Cd}(\text{NH}_2(\text{CH}_2)_6\text{NH}_2)\text{Ni}(\text{CN})_4 \cdot \text{o-CH}_3\text{C}_6\text{H}_4\text{NH}_2$. In *Clathrate Compounds, Molecular Inclusion Phenomena, and Cyclodextrins: Proceedings of the Third International Symposium on Clathrate Compounds and Molecular Inclusion Phenomena and the Second International Symposium on Cyclodextrins, Tokyo, Japan, July 23–27, 1984*, 351–357. Springer Netherlands.

(44) Yaghi, O.M.; Kalmutzki, M.J.; Diercks, C. *Introduction to Reticular Chemistry: Metal-organic Frameworks and Covalent Organic Frameworks*. **2019**, John Wiley & Sons.

(45) Nishikiori, S.I.; Iwamoto, T. 1984. Crystal Structure of Hofmann-dma-type Benzene Clathrate bis (dimethylamine) cadmium (II) tetracyanonickelate (II)-benzene (2/1). *Chem. Lett.*, **1984**, *13*, 319–322.

(46) Kawata, S.; Kitagawa, S.; Kumagai, H.; Kudo, C.; Kamesaki, H.; Ishiyama, T.; Suzuki, R.; Kondo, M.; Katada, M. Rational Design of A Novel Intercalation System. Layer-gap Control of Crystalline Coordination Polymers, $\{[\text{Cu}(\text{CA})(\text{H}_2\text{O})_m](\text{G})\}_n$ ($m = 2$, $\text{G} = 2$, 5-Dimethylpyrazine and Phenazine; $m = 1$, $\text{G} = 1,2,3,4,6,7,8,9$ -Octahydrophenazine). *Inorg. Chem.* **1996**, *35*, 4449–4461.

(47) ZareKarizi, F.; Joharian, M.; Morsali, A. Pillar-layered MOFs: Functionality, Interpenetration, Flexibility and Applications. *J. Mater. Chem. A*, **2018**, *6*, 19288–19329.

(48) Chun, H.; Dybtsev, D.N.; Kim, H.; Kim, K. Synthesis, X-ray Crystal Structures, and Gas Sorption Properties of Pillared Square Grid Nets Based on Paddle-wheel Motifs: Implications for Hydrogen Storage in Porous Materials. *Chem. Eur. J.* **2005**, *11*, 3521–3529.

(49) Choi, E. Y.; Barron, P. M.; Novotny, R. W.; Son, H. T.; Hu, C.; Choe, W. Pillared Porphyrin Homologous Series: Intergrowth in Metal-Organic Frameworks. *Inorg. Chem.* **2009**, *48*, 426–428.

(50) Amiri, N.; Bourguiba, M.; Guergueb, M.; Chevreux, S.; Nasri, H. Synthesis, Molecular Structure, Spectroscopic Characterization and Dielectric Properties of New Cobalt (II) Meso-Tetraphenylporphyrin-Based Coordination Complex. *Inorg. Chem. Commun.* **2020**, *118*, 107995.

(51) Armillotta, F.; Bidoggia, D.; Biasin, P.; Annese, A.; Cossaro, A.; Verdini, A.; Floreano, L.; Peressi, M.; Vesselli, E. Spectroscopic Fingerprints of Iron-Coordinated Cobalt and Iron Porphyrin Layers on Graphene. *Cell Rep.* **2023**, *4*, 101378.

(52) Moroni, M.; Roldan-Molina, E.; Vismara, R.; Galli, S.; Navarro, J. A. Impact of Pore Flexibility in Imine-Linked Covalent Organic Frameworks on

Benzene and Cyclohexane Adsorption. *ACS Appl. Mater. Interfaces* **2022**, *14*, 40890–40901.

(53) Das, P.; Mandal, S. K. A Dual-Functionalized, Luminescent and Highly Crystalline Covalent Organic Framework: Molecular Decoding Strategies for Vocs and Ultrafast TNP Sensing. *J. Mater. Chem. A*, **2018**, *6*, 16246–16256.

(54) Chang, J.; Chen, F.; Li, H.; Suo, J.; Zheng, H.; Zhang, J.; Wang, Z.; Zhu, L.; Valtchev, V.; Qiu, S.; Fang, Q. Three-Dimensional Covalent Organic Frameworks with nia Nets for Efficient Separation of Benzene/Cyclohexane Mixtures. *Nat. Commun.* **2024**, *15*, 813.

(55) Yan, J.; Sun, H.; Wang, Q.; Lu, L.; Zhang, B.; Wang, Z.; Guo, S.; Han, F. Covalent Triazine Frameworks for the Dynamic Adsorption/Separation of Benzene/Cyclohexane Mixtures. *New J. Chem.* **2022**, *46*, 7580–7587.

(56) Rong, M.; Yang, L.; Wang, L.; Xing, H.; Yu, J.; Qu, H.; Liu, H. Fabrication of Microporous Amino-Linked Polymers with Tunable Porosity toward Highly Efficient Adsorption of CO₂, H₂, Organic Vapor, and Volatile Iodine. *Ind. Eng. Chem. Res.* **2019**, *58*, 17369–17379.

(57) Li, G.; Zhang, B.; Yan, J.; Wang, Z. Tetraphenyladamantane-Based Polyaminals for Highly Efficient Captures of CO₂ And Organic Vapors. *Macromolecules* **2014**, *47*, 6664–6670.

(58) Chen, T.; Zhang, W.; Li, B.; Huang, W.; Lin, C.; Wu, Y.; Chen, S.; Ma, H. Adsorptive Separation of Aromatic Compounds from Alkanes by π - π Interactions in a Carbazole-Based Conjugated Microporous Polymer. *ACS Appl. Mater. Interfaces* **2020**, *12*, 56385–56392.

(59) Tan, H.; Chen, Q.; Chen, T.; Liu, H. Selective Adsorption and Separation of Xylene Isomers and Benzene/Cyclohexane with Microporous Organic Polymers POP-1. *ACS Appl. Mater. Interfaces* **2018**, *10*, 32717–32725.

(60) Macreadie, L.K.; Mensforth, E.J.; Babarao, R.; Konstantas, K.; Telfer, S.G.; Doherty, C.M.; Tsanaktisidis, J.; Batten, S.R.; Hill, M.R. CUB-5: A Contoured Aliphatic Pore Environment in a Cubic Framework with Potential for Benzene Separation Applications. *J. Am. Chem. Soc.* **2019**, *141*, 3828–3832.

(61) Ma, F. J.; Liu, S. X.; Liang, D. D.; Ren, G. J.; Wei, F.; Chen, Y. G.; Su, Z. M. Adsorption of Volatile Organic Compounds in Porous Metal-Organic Frameworks Functionalized by Polyoxometalates. *J. Solid State Chem.* **2011**, *184*, 3034–3039.

(62) Zeng, M. H.; Tan, Y. X.; He, Y. P.; Yin, Z.; Chen, Q.; Kurmoo, M. A Porous 4-Fold-Interpenetrated Chiral Framework Exhibiting Vapochromism, Single-Crystal-to-Single-Crystal Solvent Exchange, Gas Sorption, and a Poisoning Effect. *Inorg. Chem.* **2013**, *52*, 2353–2360.

(63) Kondo, A.; Suzuki, T.; Kotani, R.; Maeda, K. Liquid/Vapor-Induced Reversible Dynamic Structural Transformation of a Three-Dimensional Cu-Based MOF To a One-Dimensional MOF Showing Gate Adsorption. *Dalton Trans.* **2017**, *46*, 6762–6768.

(64) Myers, A.L.; Prausnitz, J.M. Thermodynamics of Mixed-gas Adsorption. *AIChE Journal* **1965**, *11*, 121–127.

(65) Addicoat, M. A.; Fukuoka, S.; Page, A. J.; Irls, S. Stochastic Structure Determination for Conformationally Flexible Heterogenous Molecular Clusters: Application to Ionic Liquids. *J. Comput. Chem.* **2013**, *34*, 2591–2600.

(66) Addicoat, M. A.; Vankova, N.; Akter, I. F.; Heine, T. Extension of the Universal Force Field to Metal-Organic Frameworks. *J. Chem. Theory Comput.* **2014**, *10*, 880–891.

(67) Grimme, S.; Bannwarth, C.; Shushkov, P. A Robust and Accurate Tight-Binding Quantum Chemical Method for Structures, Vibrational Frequencies, and Noncovalent Interactions of Large Molecular Systems Parametrized for All spd Block Elements ($Z = 1$ –86). *J. Chem. Theory Comput.* **2017**, *13*, 1989–2009.

