Supplemental information

Ether-linked porphyrin covalent organic framework with broadband optical switch

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**Supplemental Figures**

**Figure S1.** Theoretical structural modeling, Related to Figure 1 and STAR Methods. Structural modeling and the optimized structure of COF-Pors.

**Figure S2.** Solid-state $^{13}$C CP-MAS NMR spectrum, Related to Figure 1. Solid-state NMR spectrum of COF-Pors. Spinning sidebands are denoted with asterisks (MAS frequency: 8kHz).
**Figure S3.** FTIR spectra, Related to Figure 1.
FTIR spectra of F-Por, HO-Por, and COF-Pors.
**Figure S4.** XPS spectra. Related to Figure 1.

XPS wide-scan spectra of (A) F-Por and (B) COF-Pors.

(C) F1s core level XPS spectrum of F-Por.

(D) F1s, (E) N1s and (F) C1s core level XPS spectra of COF-Pors.
Figure S5. Porosity of COF-Pors, Related to Figure 2.

N$_2$ physisorption isotherms of COF-Pors at 77 K; inset: pore width distribution histogram of COF-Pors calculated from DFT fitting of the adsorption branch of the N$_2$ adsorption isotherm.
Figure S6. Thermal Stability, Related to Figure 3. TGA curves of COF-Pors.
Figure S7. EPR spectra, Related to Figure 3.
EPR spectra of COF-Pors before and under illumination. The laser wavelength, energy and illumination time for EPR measurement are 532 nm, 12 W and 1 minutes, respectively.
**Figure S8.** HR-TEM image, Related to Figure 2.
HR-TEM image and the corresponding lattice distances of COF-Pors.

**Figure S9.** TEM and EDX mapping images, Related to Figure 2.
TEM image, EDX mapping images with N (red color), O (yellow color), C (green color) and the corresponding overlapping image of COF-Pors.
Figure S10. SEM images, Related to Figure 2.
SEM images of COF-Pors.
Figure S11. FESEM and EDX mapping images, Related to Figure 2.
FESEM image and EDX mapping images with N (red color), O (yellow color), C (green color) of COF-Pors.
Figure S12. Transient absorption spectra, Related to Figure 3.
(A, B) The 2D and 3D TA spectra of COF-Pors in DMF at the indicated delay times ($\lambda_{ex}$=400 nm).
(C) The time profile of COF-Pors at 700 nm.
**Figure S13.** Nonlinear optical properties of F-Por and HO-Por, Related to Figure 4.

Typical open-aperture Z-scan data for the samples dispersed in DMF under excitation of 6 ns pulses at 532 nm and 1064 nm.
**Supplemental Table**

**Table S1.** Unit cell parameters and fractional atomic coordinates for COF-Pors, Related to STAR Methods, Figure 1 and Figure S1.

COF-Pors-unit, P1 symmetry a=20.0 Å, b=19.5 Å, c=3.7 Å. α=β=γ=90°

| ATOM | x       | y       | z      |
|------|---------|---------|--------|
| C    | 11.10074055554926 | 15.20396107163578 | 3.59409712131163 |
| C    | 13.13921772536014 | 13.17626264641856 | 3.50949340806344 |
| C    | 15.69605486075899 | 14.52115853096371 | 3.2255360125875 |
| N    | 15.25882619320084 | 17.36932529105805 | 3.08224704638018 |
| C    | 12.41407344444924 | 17.7736531543827 | 3.3024367113163 |
| C    | 13.22924822865726 | 27.46879646805833 | 2.78744360281510 |
| C    | 11.18732501358125 | 25.43350850588066 | 2.57956231134056 |
| C    | 12.44042814891378 | 22.86625472534427 | 3.1029182035873 |
| N    | 15.23082909700081 | 23.31977384351866 | 3.59218170058052 |
| C    | 15.72625645276560 | 26.14455402961204 | 3.4570821712991 |
| C    | 11.00742454724016 | 20.32996836840903 | 3.2085969420490 |
| C    | 25.22352055717060 | 25.16413666580367 | 5.1360563352139 |
| C    | 23.18537000831110 | 27.18254184501628 | 5.3513656197552 |
| C    | 20.71265601825497 | 26.02088657631966 | 4.37852518723771 |
| N    | 21.16518652809680 | 23.28037194832276 | 3.63144326565207 |
| C    | 23.97330319236793 | 22.79259030593159 | 4.0290180462345 |
| C    | 18.2412436610604 | 27.51275978417474 | 4.00543682105216 |
| C    | 23.13882962474695 | 13.53733593879794 | 1.8772960379344 |
| C    | 25.1755691256877 | 15.58570725774724 | 1.38303806940866 |
| C    | 23.96310923468621 | 17.97091776046679 | 2.50897282971204 |
| C    | 21.19406218579358 | 17.42105712385768 | 3.0044876534634 |
| C    | 20.68764205179941 | 14.67685400937527 | 2.35539107611170 |
| C    | 18.27465822712329 | 13.16659831111533 | 2.97878450324225 |
| C    | 25.41006169685945 | 20.38522687644054 | 3.24787963261248 |
| C    | 18.3088030541785 | 30.42887656410661 | 4.12927913259261 |
| C    | 28.32960638145455 | 20.37925666469385 | 3.23042984110305 |
| C    | 8.08771979717310 | 20.38014010859514 | 3.2609763494574 |
| C    | 17.98460933646842 | 10.725884797418340 | 2.83530218796368 |
| C    | 20.86628775511132 | 31.82568843911372 | 4.10572372314591 |
| C    | 20.94411296594710 | 34.73401750656039 | 4.10455718551514 |
| C    | 18.4659883112055 | 36.2551943983850 | 4.08326517072303 |
| C    | 15.91009857120293 | 34.86881191672058 | 4.1969409657336 |
| C    | 15.83232372447434 | 31.95936628947514 | 4.23209837705279 |
| C    | 29.78434329999307 | 17.87177589658969 | 2.95067024782745 |
| C    | 32.69405932814974 | 17.86400356831088 | 2.93140162754719 |
| C    | 34.1592039377783 | 20.36027679406635 | 3.21948962508119 |
| C    | 32.71313473641718 | 22.86650612127985 | 3.5149506139626 |
| C    | 29.80280678028019 | 22.87774927173791 | 3.50220435267467 |
