(Electronic Supplementary Information)

Thiazolo[5,4-d]thiazole-Bridged Porphyrin Organic Framework as Promising Nonlinear Optical Material

Mahalaxmi Samal,^a Sreeramulu Valligatla,^b Nabil A. Saad,^c M. Veeramohan Rao,^d D. Narayana Rao,^c Rojalin Sahu^{*,a} and Bishnu P. Biswal^{*,e,f}

^aDepartment of Chemistry, School of Applied Sciences, Kalinga Institute of Industrial Technology (KIIT), Deemed to be University, Bhubaneswar-24, Odisha, India. E-mail: <u>rsahufch@kiit.ac.in</u>; Tel: (+91)-9778127994; Fax: (+91)-674 2725113.
^bInstitute for Integrative Nanosciences, IFW- Dresden, 01069, Dresden, Germany.
^cSchool of Physics, University of Hyderabad, Hyderabad-500046, India.
^dDepartment of Physics, Pondicherry University, Pondicherry - 606015, India.
^eFaculty of Chemistry and Food Chemistry, Center for Advancing Electronics Dresden, Technische Universitat Dresden, 01062, Dresden, Germany.
^fPresent Address: Max-Planck-Institute for Solid State Research, Heisenbergstraße 1, 70569 Stuttgart, Germany.

E-mail: <u>b.biswal@fkf.mpg.de</u>.

Contents

Section S1: General information	
Section S2: Synthetic procedures	3
Section S3: Characterization details of Por-TzTz-POF	
Section S4: Morphology (SEM and TEM) and XPS	
Section S5: Nonlinear optical (NLO) properties	
Section S6: References	

Section S1: General information

General remarks: All solvents, reagents and chemicals were purchased form Sigma Aldrich and used without further purification. Meso-tetrakis(4-bromophenyl)porphyrin, 5,10,15,20-tetrakis(4aminophenyl)-21H,23H-porphyrin (TAPP) was purchased from PorphyChem. Silica gel for column chromatography was used from Sigma Aldrich (pore size 60 Å, 70 - 230 mesh, $63 - 200 \mu$ m). Powder X-ray diffraction (PXRD) patterns were recorded on STOE STADI P diffractometer for Cu Ka radiation ($\alpha = 1.5406$ Å), with a scan speed of 1° min⁻¹ and a step size of 0.02° in 2 θ . NMR data were recorded on a Bruker AV 300 spectrometer operating at 300 MHz for ¹H with standard Bruker plus programs at room temperature. Chemical shifts δ are given in ppm relative to TMS; coupling constants J are given in Hertz (Hz). CD_2Cl_2 , δ (¹H) = 5.32 ppm were used as solvent, lock and internal standard. ¹³C CP solid-state NMR spectra were recorded on a BRUKER Ascend 800 MHz spectrometer using a commercial 2.5 mm MAS NMR probe and operating at a resonance frequency of 201.2 MHz. The MAS frequency was 18 kHz. As external standard, adamantane was used. Ramped ¹H-¹³C cross-polarization (CP, contact time: 4 ms) and SPINAL ¹H-decoupling during the signal acquisition was applied. The mass spectrometry analysis was performed on a Bruker Autoflex Speed MALDI TOF MS (Bruker Daltonics, Bremen, Germany) using dithranol as matrix. UV-visible spectra were measured on an Agilent Cary 5000 UV-VIS-NIR spectrophotometer using 10 mm optical-path quartz cell at room temperature. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Optics ALPHA-E spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory in the 600–4000 cm⁻¹. Thermogravimetric analyses (TGA) were carried out on a TG50 analyzer (Mettler-Toledo) under N2 atmosphere with a heating rate of 10 °C min⁻¹. Low-pressure volumetric gas adsorption measurements were performed at 77 K for N₂, maintained by a liquid nitrogen bath, with pressures ranging from 0 to 760 Torr on a Micromeritics, TriStar II Plus automated, three-station, surface area and porosity analyzer. The Brunauer-Emmett-Teller surface area was calculated within the relative pressure range 0.01 to 0.2. Total volume was calculated at P/Po = 0.99. Non-local Density Functional Theory (NLDFT) cylindrical-slit adsorption kernel for carbon was used to determine the pore size distributions. Prior to physisorption measurements the samples were evacuated at 120°C for 12 h. SEM images were obtained with a Zeiss DSM 950 scanning electron microscope and FEI, QUANTA 200 3D Scanning Electron Microscope with tungsten filament as electron source operated at 10 kV. The samples were sputtered with Au (nano-sized film) prior to imaging by a SCD 040 Balzers Union. TEM images were recorded using FEI Tecnai G2 F20 X-TWIN TEM at an accelerating voltage of 200 kV. For TEM, the samples were sonicated for 15 min in 2-propanol, followed by drop casting the sample on carbon coated copper TEM grids (TED PELLA, INC. 200 mesh). Similar methodology was followed for SEM sample preparation, where in the samples were coated on Silicon Oxide surface. Steady-state and time-resolved

emission data was collected at room temperature using an Edinburgh FLS980 spectrometer. For steadystate emission, samples were excited using light output from a housed 450 W Xe lamp passed through a single grating (1800 l/mm, 250 nm blaze) Czerny-Turner monochromator and finally a bandwidth slit. Emission from the sample was passed through a double grating (1200 l/mm, 500 nm blaze) Czerny-Turner monochromator (appropriate bandwidth) and finally detected by a cooled microchannel plate photomultiplier tube (MCP-PMT) detector. The dynamics of emission decay was monitored by using the FLS980's time-correlated single-photon counting capability (1024 channels; 100 ns window) with data collection for 5000 counts. Excitation was provided by an Edinburgh EPL-375 picosecond pulsed laser diode (375 \pm 6 nm, pulse width - 68 ps) and a cooled microchannel plate photomultipler tube (MCP-PMT) was used as the detector. Kinetics were fit with a (bi)exponential function by using the Edinburgh software package, whenever required. X-ray photoelectron spectroscopy (XPS) measurements were performed with an Axis Ultra system from Kratos equipped with a monochromatized Al Ka source. Detail scans were acquired with a pass energy of 20 eV. The peaks were fitted after subtraction of a Shirley background. A Gauss/Lorentz ratio of 30% was used for all peaks and the full width half maximum was used as a free fitting parameter. Elemental analysis (EA) was carried out with an Elementar vario EL (Elementar Analysensysteme, Hanau, Germany).

Section S2: Synthetic procedures

5,10,15,20-tetrakis(4-formylphenyl)-21*H***,23***H***-porphyrin (TFPP):</u> TFPP has been synthesized using our reported procedure.^{S1} To a solution of Meso-tetrakis(4-bromophenyl)porphyrin (500 mg, 0.54 mmol) in dry diethylether (60 mL), n-buthyllithium (5.4 mL, 8.6 mmol) was added at -50°C dropwise under argon. The resulting solution was stirred for 30 min at -50 °C, then warmed up slowly to 0 °C, and stirred for 8 h more. After cooling down to -50°C, dry DMF (10 mL) was added. The temperature was kept for 1 h, then the resulting mixture was warmed up to room temperature and stirred overnight. 5% HCl (350 mL) was added to quench the reaction. After 30 min, NH₄OH was added at 0 °C, and the mixture was extracted with chloroform and evaporated. The crude product was subjected to column chromatography with dichloromethane (DCM) as eluent, to give TFPP as dark purple solid (137 mg, 35% yield). ¹H NMR (CD₂Cl₂) \delta (ppm): 10.39 (s, 4H), 8.87 (s, 8H), 8.42 (d, 8H), 8.30 (d, 8H), -2.82 (s, 2H). HR-MALDI-TOF MS for C₄₈H₃₀N₄O₄ (calcd. 726.2267):** *m/z* **= 726.2256 ([M + H]⁺). FT-IR, (cm⁻¹): 3313 (NH), 3107 (CHAr), 1694 (C=O), 1597 (C=Cphenyl), 1560 (C=Cpyrrole), 1469 (C=N), 1378 (=C-N), 1166 (CHpyrrole), 965 (CH porp. ring), 801 (CH pyr. ring), 728 (NH bending).**



Figure S1. High resolution-MALDI-TOF MS spectra of TFPP with DCTB as matrix.



Figure S2. ¹H NMR spectra of TFPP recorded in CD₂Cl₂.

Synthesis of Por-TzTz-POF: A PYREX[®] tube (o.d. × i.d. = $1 \times 0.8 \text{ cm}^2$ and length 18 cm) was charged with 5,10,15,20-tetrakis(4-formylphenyl)-21*H*,23*H*-porphyrin (TFPP) (30.2 mg, 41.6 µmol, 1 equiv.), dithiooximide (DTO) (10 mg, 83.2 µmol, 2 equiv.) and 2 mL of nitrobenzene. This mixture was sonicated for 10 min. in order to get a homogenous dispersion. The tube was then flash frozen at 77 K (liquid N₂ bath) and degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum and then heated at 150 °C for 4 days. A brownish-black precipitate was collected by filtration and washed with ethanol, *N*,*N'*-dimethylacetamide (DMAc) and acetone several times until the filtrate became colorless, dried at 120 °C under vacuum for 12 h to obtain Por-TzTz-POF (29 mg) in 72 % isolated yield. Anal. Calcd. (%) for (C₅₂H₂₆N₈S₄)n: C, 70.10; H, 2.92; N, 12.58; S, 14.37. Found (%): C, 69.43; H, 4.41; N, 10.72; S, 9.61.

Synthesis of Por-C=N-COF: Por-C=N-COF has been synthesized using our previously reported procedure.^{S1} A PYREX[®] tube (o.d. × i.d. = $1 \times 0.8 \text{ cm}^2$ and length 18 cm) was charged with 5,10,15,20-tetrakis(4-formylphenyl)-21*H*,23*H*-porphyrin (TFPP) (21.5 mg, 1 eq.), 5,10,15,20-tetrakis(4-aminophenyl)-21*H*,23*H*-porphyrin (TAPP) (20 mg, 1 eq.) in *o*-dichlorobenzene and n-butanol (1: 1 by vol., 1.5 ml) in presence of 6M aqueous acetic acid (0.1 ml). This mixture was sonicated for 5 min. in order to get a homogenous dispersion and the tube was then flash frozen at 77 K (liquid N₂ bath), degassed by three freeze-pump-thaw cycles. Finally sealed under vacuum and then heated at 120 °C for 3 days. A brownish coloured precipitate was collected by filtration and washed with N,N'-dimethylacetamide (DMAc) ethanol, tetrahydrofuran, and acetone several times until the filtrate became colourless, dried at 100 °C under vacuum for about 12 h to obtain Por-COF-HH as light brown solid (32 mg, 77% yield). Anal. Calcd. (%) for (C₉₂H₆₈N₁₂)_n: C, 82.36; H, 5.11; N, 12.53. Found (%): C, 76.34; H, 4.63; N, 11.97.





Figure S3. Comparison of FT-IR spectra of Por-TzTz-POF and respective starting materials (TFPP and DTO).



Figure S4. Thermogravimetric analysis (TGA) profiles of Por-TzTz-POF.



Figure S5. Pore size distributions of Por-TzTz-POF calculated using NLDFT method.



Section S-4: Morphology (SEM and TEM)

Figure S6. a, b) SEM images and c, d) TEM images of Por-TzTz-POF at different magnifications.



Figure S7. X-ray photoelectron spectral (XPS) analysis of Por-C=N-COF^{S1} with survey scans on the top and high resolution scans on the bottom. Indium comes from the substrate. Some oxygen and carbon impurity might also be present as contamination of the Indium foil.

XPS analysis of Por-TzTz-POF and Por-C=N-COF indicates that both contains free base porphyrin, three prominent nitrogen species can be identified corresponding to the pyrolic and iminic N of porphyrin and the COF imine (C=N) bond respectively. A fourth, albeit less intense N species corresponding to a binding energy of 402.91 eV can also be observed that possibly corresponds to some oxidized N (NOx) impurities. However, in case of Por-TzTz-POF, majorly one type of S atom is present ascribe to the TzTz unit along with some oxidized S (SOx) impurities peak and that results poor fitting of the S 2p.



Figure S8. X-ray photoelectron spectral (XPS) analysis of Por-TzTz-POF with survey scans on the top and high-resolution scans at the bottom. Indium comes from the substrate. Some oxygen and carbon impurity might also be present as contamination of the Indium foil.



Figure S9. Ball and stick models of the energy optimized primary structural unit of a) Por-TzTz-POF and b) Por-C=N-COF, the dihedral angles has been marked to show case the linkage planarity of TzTz-phenyl and imine (C=N)-phenyl respectively. The optimized structural models were constructed using BIOVIA Materials Studio 2017 (17.1.0.48. Copyright © 2016 Dassault Systèmes) suite.

Section S-5: Nonlinear optical (NLO) properties

Third order nonlinear optical properties of Por-C=N-COF and Por-TzTz-POF were measured in the dispersion state [1 mg of respective solid material in 10 ml of 2-propanol; Por-C=N-COF: Molecular Weight: 1325.57 and concentration is 7.544×10^{-5} mol/L; Por-TzTz-POF: Molecular Weight: 890.15 g/mol and concentration is 1.1234×10^{-4} mol/L] using Z-scan technique with nanosecond (ns) laser pulses. The ns laser is a frequency doubled, Q-switched Nd: YAG (INDI-40, Spectra-Physics) laser, delivering 6 ns pulses at 532 nm with a repetition rate of 10 Hz. The very popular Z-scan technique, which is a focussed single beam method and translation of the sample across the focal point, was used for measuring both nonlinear refraction and nonlinear absorption.^{\$2, \$3} A lens with focal length of 12 cm was used to focus the Gaussian beam and the sample moved through the beam waist of the laser beam over the length of 60 mm. At the focal point, the sample experiences maximum pump intensity and which gradually decreases in either direction from the focus. The sample solution taken in 1 mm cuvette is smaller than the Rayleigh range of the focussed beam, which is calculated to be ~ 4 mm. The five level rate equations were used to fit the open aperture data in ns region.

$$\frac{\partial N_0}{\partial t} = -\frac{\sigma_o I N_0}{h\omega} - \frac{\beta I^2}{2h\omega} + \frac{N_1}{\tau_{S_1}} + \frac{N_3}{\tau_{t_1}}$$
(1)

$$\frac{\partial N_1}{\partial t} = \frac{\sigma_o I N_0}{h\omega} - \frac{\sigma_1 I N_1}{h\omega} - \frac{N_1}{\tau_{s_1}} - \frac{N_1}{\tau_{isc}} + \frac{N_2}{\tau_{s_n}}$$
(2)

$$\frac{\partial N_2}{\partial t} = \frac{\sigma_1 I N_1}{h\omega} + \frac{\beta I^2}{2h\omega} - \frac{N_2}{\tau_{s_n}}$$
(3)

$$\frac{\partial N_3}{\partial t} = -\frac{\sigma_2 I N_3}{h\omega} - \frac{N_3}{\tau_{t_1}} + \frac{N_1}{\tau_{isc}} + \frac{N_4}{\tau_{t_n}} \tag{4}$$

$$\frac{\partial N_4}{\partial t} = -\frac{\sigma_2 I N_3}{h\omega} - \frac{N_4}{\tau_{t_n}}$$
(5)

$$N = N_1 + N_2 + N_3 + N_4 + N_{T_1}$$

Where, N_j is the population per cubic centimetre of state S_j , while j = 1, 2, 3; h is the reduced Planck constant, ω is the laser frequency and τ_{sl} is the lifetime for state S_i , while i = 1, n.

$$I(Z,t) = I_{oo} \left(\frac{\omega_o^2}{\omega^2(Z)}\right) \cdot \exp\left(\frac{-2r^2}{\omega^2(Z)}\right) \cdot \exp\left(\frac{-t^2}{\tau_p^2}\right)$$
$$\omega(Z) = \omega_o \left[1 + \left(\frac{Z}{Z_o}\right)^2\right]^{\frac{1}{2}}$$
$$Z_o = \frac{\pi \omega_o^2}{\lambda}$$

 α_0 is linear absorption coefficient, β is the two photon absorption coefficient (TPA), Z_0 is Rayleigh range ω_0 is the beam waist at focus, I is the intensity as a function of *r*, *t*, and *z*, I_{00} is peak intensity at the focus of the Gaussian beam, and τ_p is the input pulse width used. The differential equation is solved numerical integration. The differential equation is integrated temporally and spatially. Assuming the input beam to be a Gaussian, the limits of integration for *r*, *t*, and *z* are varied from 0 to ∞ , $-\infty$ to ∞ , and 0 to L (length of the sample), respectively.

$$\frac{dI}{dz} = -(\beta I^2 + \sigma_0 N I + \sigma_1 N_1 I + \sigma_2 N_3 I)$$
(6)

Where, β is two-photon absorption coefficient (TPA), σ_0 is ground state absorption cross section and σ_1 is first excited state absorption cross section coefficient and σ_2 is second excited state absorption cross

$$\frac{\sigma_1}{(1+\frac{I(Z)}{I_{sat}})}$$
 and

section coefficient While modelling, we introduced the saturation for both σ_1 and β as

$$\frac{\beta}{(1+(\frac{I(Z)}{I_{sat}})^2)}$$

to explain the switching behaviour. Where I_{sat} is saturation intensity of S_n state. For porphyrins molecules, σ_1 is taken as effective excited state absorption cross section which includes the $S_1 \rightarrow S_n$ and $T_1 \rightarrow T_n$ of porphyrin molecules and β is taken as effective TPA coefficient for these compounds.

Table S1: Two photon absorption co-efficient (β), ground state (σ_0), first excited state (σ_1) and second excited state absorption coefficients (σ_2) for Por-C=N-COF and Por-TzTz-POF. σ_1/σ_0 represents the figure of merit (FoM).

Materials	β(cm/GW)	$\sigma_0 (10^{-19})(\text{cm}^2)$	$\sigma_1 (10^{-19})(\text{cm}^2)$	$\sigma_2 (10^{-19})(\text{cm}^2)$	FOM (01/00)
Por-C=N-COF ^{S1}	1040	0.58	2050	800	3534
Por-TzTz-POF	1100	1.4	7800	3500	5571

Table S2: A list of the nonlinear optical parameters of different materials including metalloporphyrins, graphene, graphene-porphyrin composites, coordination polymers (CPs or MOFs) and COFs measured using Z-scan technique.

Materials	Measurement condition	rement condition NLO parameters	
PorCOF-ZnNi	Z-scan, 532 nm, 6 ns	4170 cm/GW, FoM = 3762	S 1
PorCOF-ZnCu	Z-scan, 532 nm, 6 ns	4470 cm/GW, FoM = 3565	S 1
3D Tetrazine chromophore MOFs (1-3)	Z-scan, 532 nm, 5 ns	$\beta = 0.28 \text{-} 0.46 \text{ cm/GW}$	S4
Nickel-p- benzenedicarboxylic acid MOF (Ni-MOF)	Z-scan, 800 nm	$\beta_{eff} = -3 \times 10^{-2} \text{ cm/GW}$	S5
Sa-TAPA COF	Z-scan, 532 nm, 10 Hz	Optical limiting threshold = 2.38 J/cm^2	S 6
Graphene	Z-scan, 532 nm, 6 ns	900 cm/GW, FoM = 5.68	S7
Graphene-Cu-porphyrin	Z-scan, 532 nm, 6 ns	4720 cm/GW, FoM = 45.78	S7
Graphene-Zn-porphyrin	Z-scan, 532 nm, 6 ns	3570 cm/GW, FoM = 43.67	S7
Cu-porphyrin	Z-scan, 532 nm, 6 ns	132 cm/GW, FoM = 19.75	S7
Zn-porphyrin	Z-scan, 532 nm, 6 ns	366 cm/GW, FoM = 25.68	S 7

Figure of merit (FoM) = σ_1/σ_0 , where, σ_1 is first excited state absorption cross-section and σ_0 is ground state absorption cross-section.

Section S-6: References

- [S1] B. P. Biswal, S. Valligatla, M. Wang, T. Banerjee, N. Momen, B. M. K. Mariserla, N. Chandrasekhar, D. Becker, M. Addicoat, I. Senkovska, R. Berger, D N. Rao, S. Kaskel, X. Feng, Angew. Chem. Int. Ed.; 2019, 58, 6896–6900.
- [S2] M. Sheik-Bahae, A. A. Said, T. Wei, D. J. Hagan, E. W. Van Stryland, IEEE J. Quantum Electron. 1990, 26, 760–769.
- [S3] V. Sreeramulu, K. K. Haldar, A. Patra, D. N. Rao, *Optics and Laser Techn.* 2016, **118**, 30333.
- [S4] J. Li, D. Jia, S. Meng, J. Zhang, M. P. Cifuentes, M. G. Humphrey, and C. Zhang, *Chem. Eur. J.* 2015, 21, 7914–7926.
- [S5] X. Jiang, L. Zhang, S. Liu, Y. Zhang, Z. He, W. Li, F. Zhang, Y. Shi, W. Lü, Y. Li, Q. Wen, J. Li, J. Feng, S. Ruan, Y.-J. Zeng, X. Zhu, Y. Lu, and H. Zhang, *Adv. Optical Mater.* 2018, 1800561.
- [S6] X. Li, Q. Gao, J. Aneesh, H.-S. Xu, Z. Chen, W. Tang, C. Liu, X. Shi, K. V. Adarsh, Y. Lu, and K. P. Loh, *Chem. Mater.* 2018, **30**, 5743–5749.
- [S7] M. B. M. Krishna, V. P. Kumar, N. Venkatramaiah, R. Venkatesan, and D. N. Rao, Appl. Phy. Lett. 2011, 98, 081106.