

Supporting Information

Synergistic Enhancement of Nonlinear Optical Limiting via In-Situ Confined Carbon Nanodots in Metal-Porphyrinic Framework Thin Film

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EXPERIMENTAL SECTION

DFT calculations:

All the calculations were performed using Gaussian 16¹. The ground-state equilibrium geometries of CDs@PIZA-1 were fully optimized using B3LYP functional and 6-31g (d, p) basis sets for C, H, N, O and Lanl2DZ for Co with D3 dispersion correction of Grimme. In order to get a deeper understanding of the wave function, Multiwfn 3.8(dev) code² and VMD³ software were used to analyze the electronic structures.

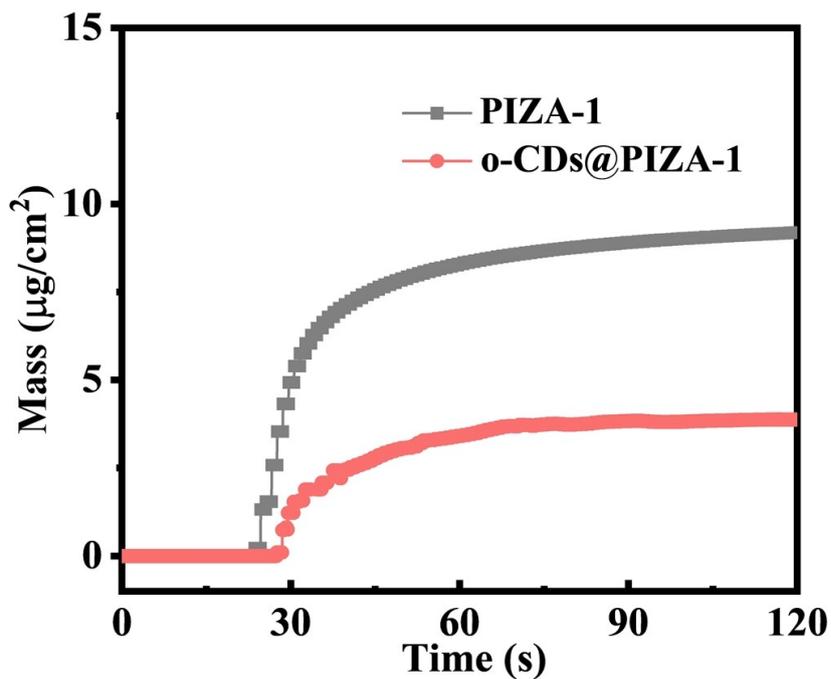


Figure S1. The mass uptakes of methanal for PIZA-1 and o-CDs@PIZA-1 thin film.

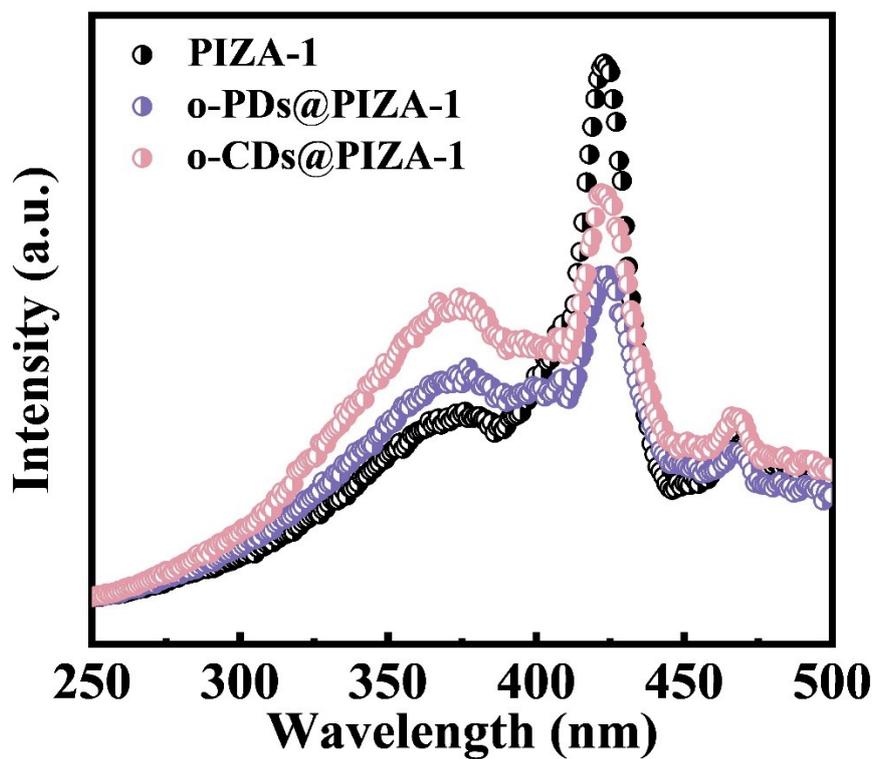


Figure S2. The PL excitation spectra of PIZA-1, o-PDs@PIZA-1 and o-CDs@PIZA-1 thin films.

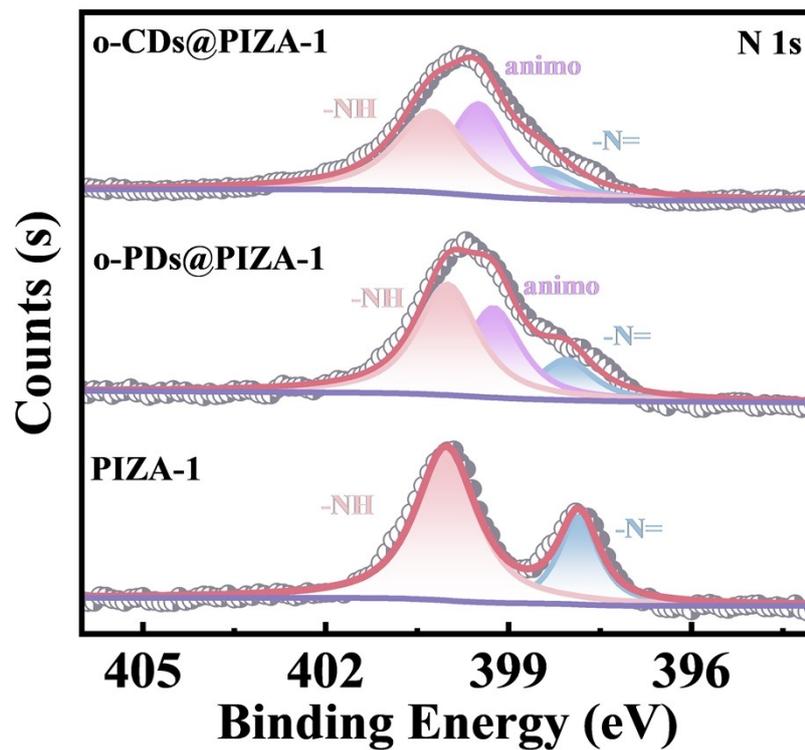


Figure S3. The N 1s XPS spectra of PIZA-1, o-PDs@PIZA-1 and o-CDs@PIZA-1 thin films.

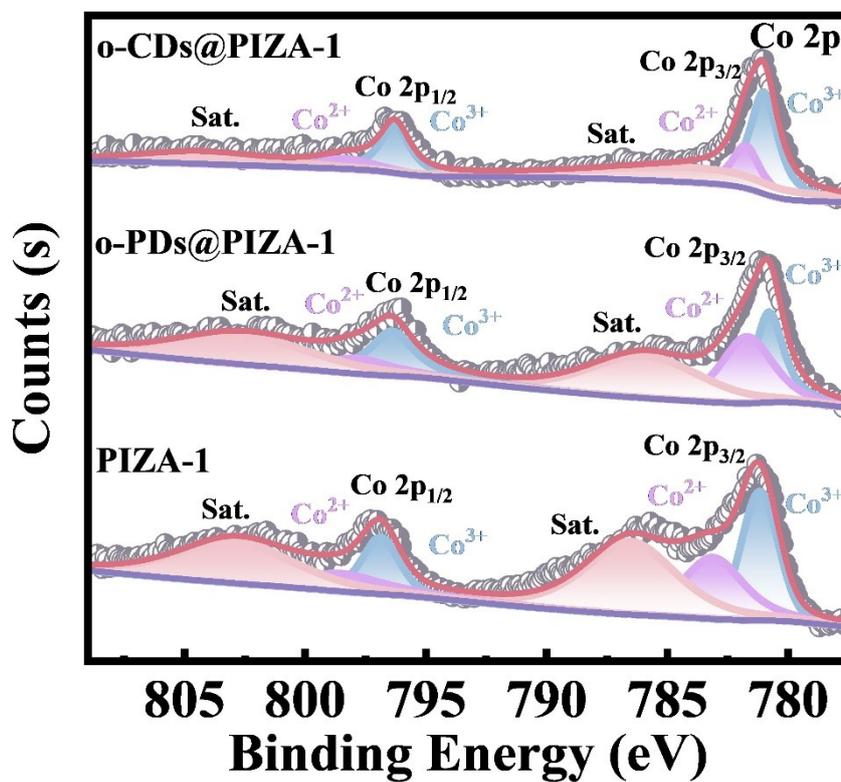


Figure S4. The Co 2p XPS spectra of PIZA-1, o-PDs@PIZA-1 and o-CDs@PIZA-1 thin films.

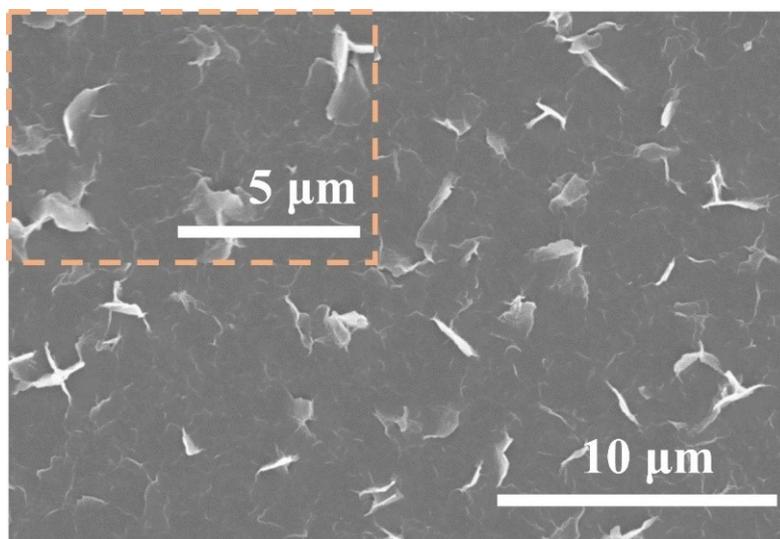


Figure S5. The SEM image of PIZA-1 thin film.

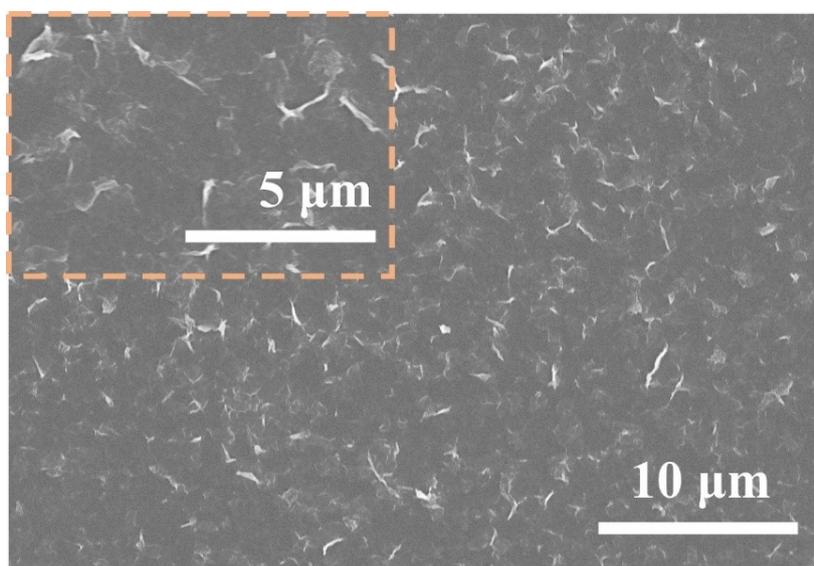


Figure S6. The SEM image of o-PDs@PIZA-1 thin film.

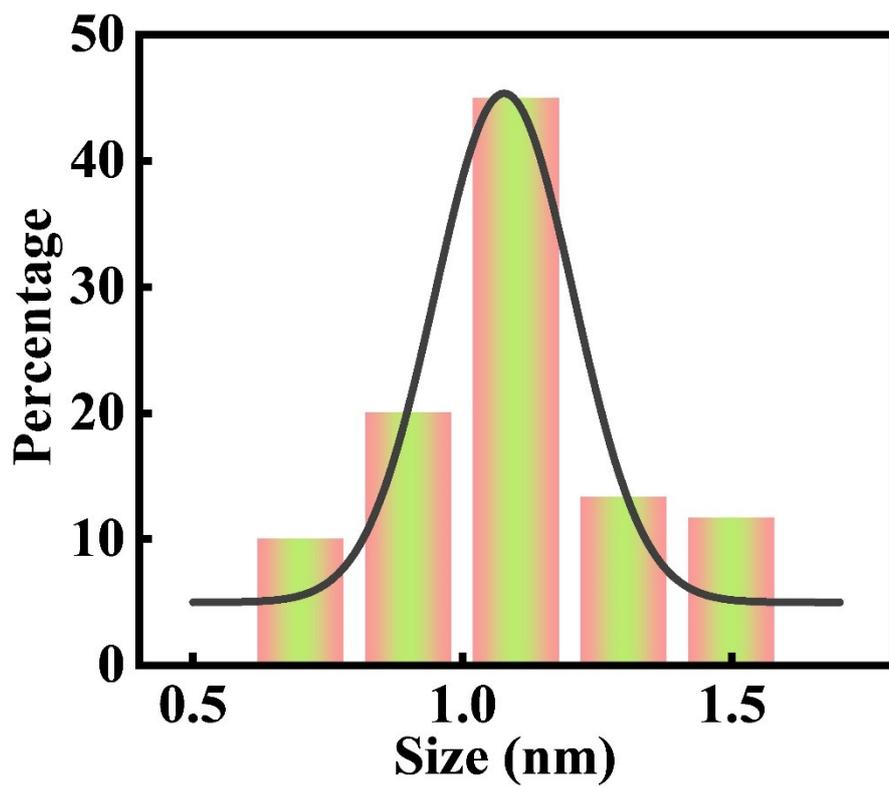


Figure S7. The size distribution of o-CDs.

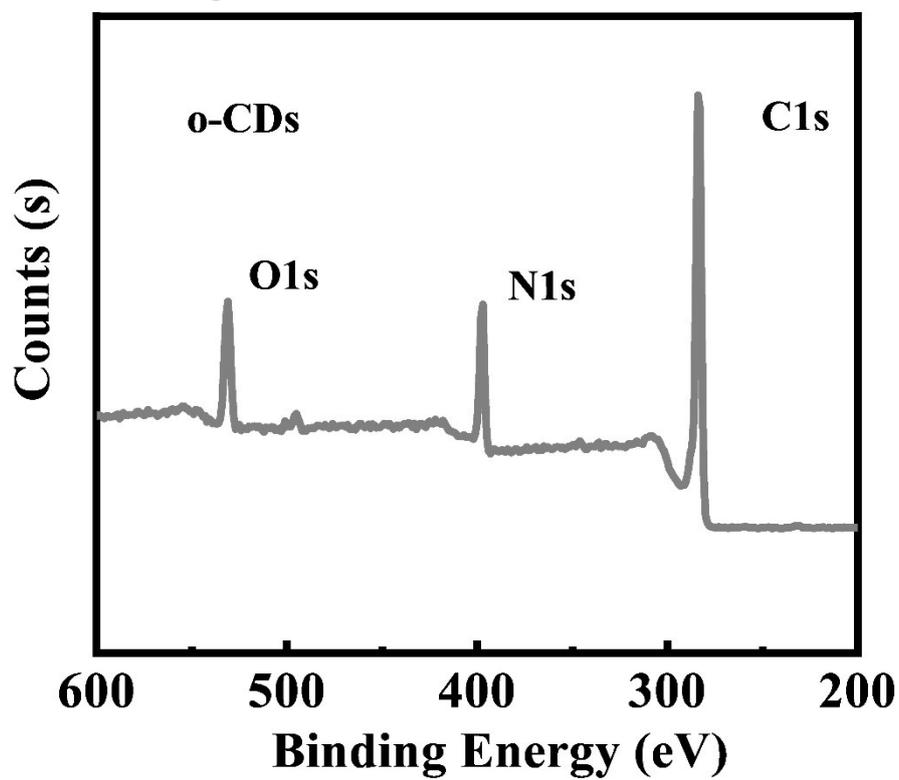


Figure S8. The survey XPS spectra of o-CDs.

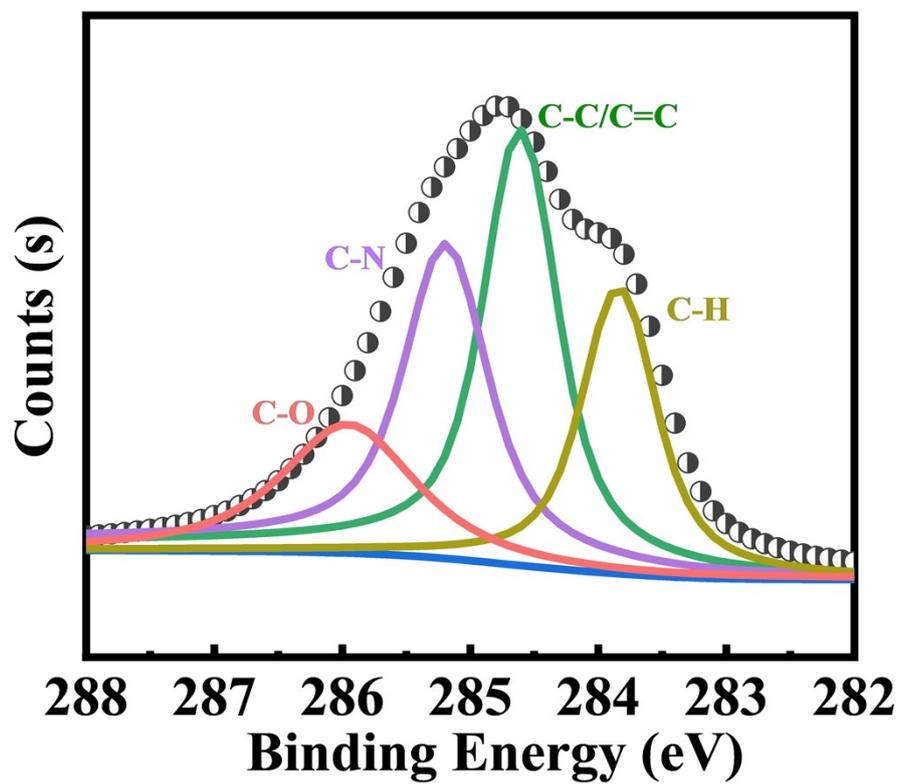


Figure S9. The high-resolution XPS spectra of o-CDs for C1s.

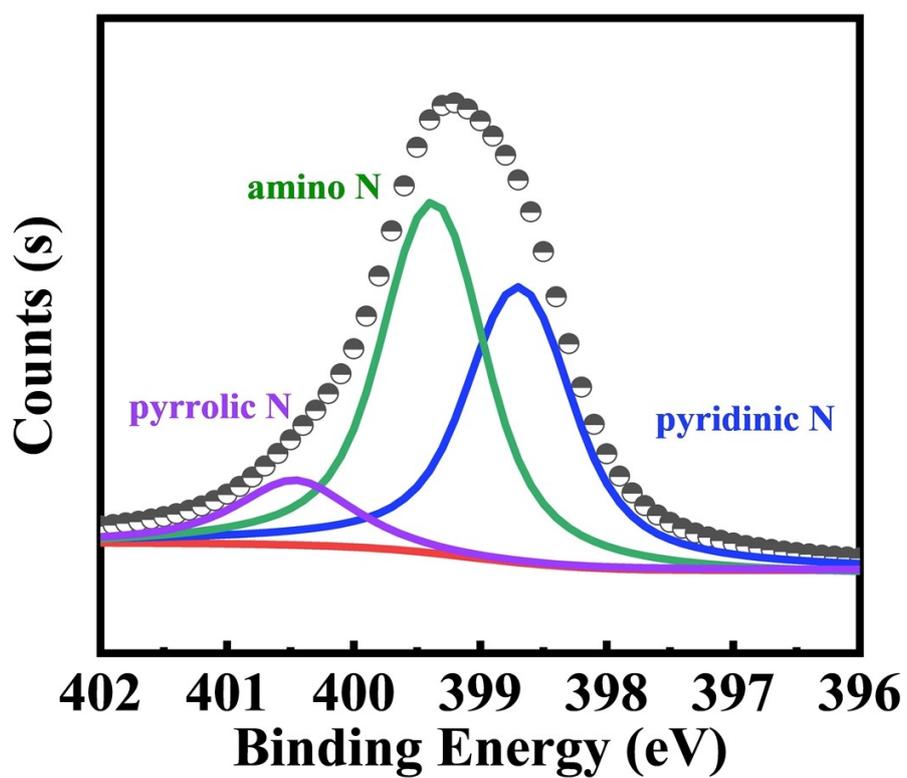


Figure S10. The high-resolution XPS spectra of o-CDs for N1s.

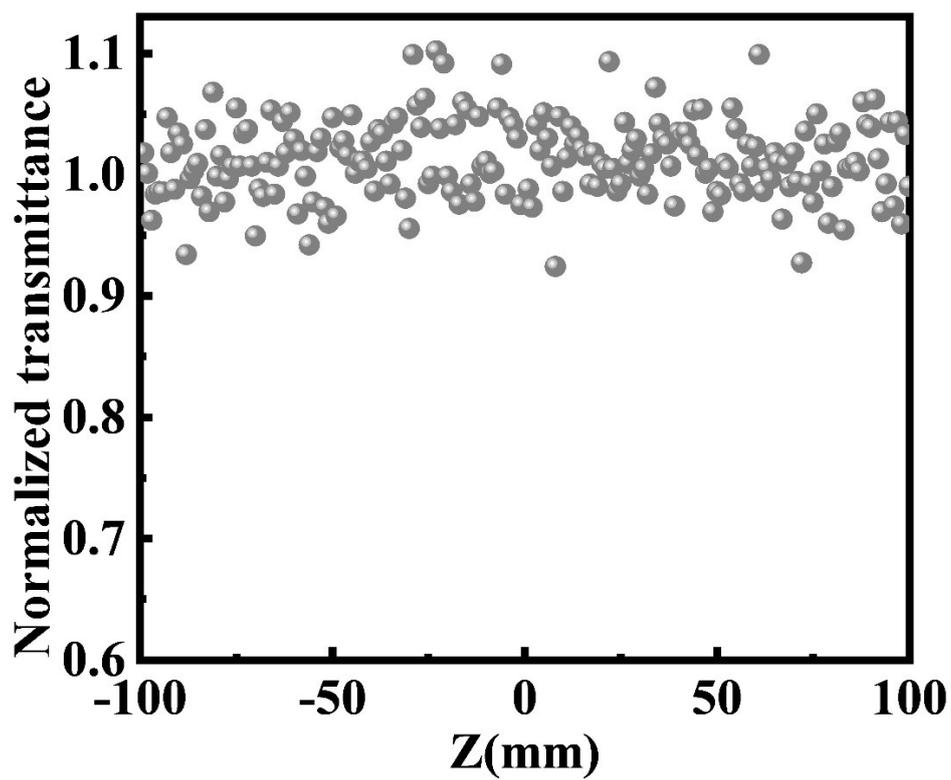


Figure S11. The open-aperture Z-scan plots of bare glass.

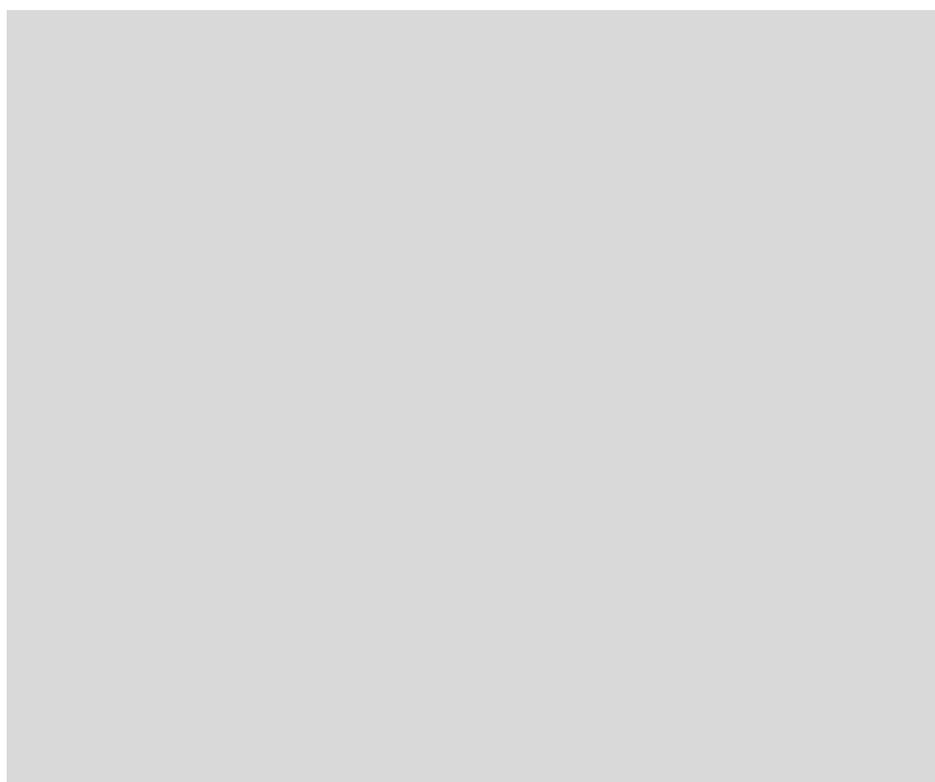


Figure S12. The open-aperture Z-scan plots of o-CDs@PIZA-1 thin film at different incident pulse energy.

Table S1. The comparison of the nonlinear absorption coefficients.

Samples	β (cm/GW)	References
o-CDs@PIZA-1 thin film	$\sim 3.1 \times 10^5$	In this work
PIZA-1 thin film	$\sim 2.16 \times 10^5$	In this work
MoS ₂ /PMMA	970.4	4
MoS ₂ -pvk	917.57	5
PFTP-RGO/PMMA	296.79	6
BP:C ₆₀	241.73	7
PF-RGO	7.07	8
Por-TzTz-POF	1100	9
Por-COF-HH	1040	10
Por-COF-ZnNi	4170	
Por-COF-ZnCu	4470	
SWNT-TPP	105	11
Mn-TMPP CPs	9	12
Zn-TMPP CPs	46	
Mn-THPP CPs	9	
Zn-THPP CPs	18	
(NH ₂) ₄ (4-TPP-Mn)	22	13
[(TBA) ₈ {(4-TPP)(Mo ₆ O ₁₈) ₄ }]	88	
[(TBA) ₈ {(4-TPP-Mn)(Mo ₆ O ₁₈) ₄ }]	98	
Co-THPP MOF	24-95	14
MQD-TPP/PMMA film	1059.17	15
TBIT-ZnPc	5.93	16

TBIT-InClPc	8.90	
TBTT-ZnPc	8.47	
TBTT-InClPc	12.10	
H ₂ TPPc	41	17
DNDs-H ₂ TPPc	58.5	
ZnTPPc	42.8	
DNDs-ZnTPPc	60.9	
Si(OH) ₂ TPPc	136	
DNDs-Si(OH) ₂ TPPc	125	
Copper porphyrin	132	18
Zinc porphyrin	366	
Pure grapheme	900	
[WS ₄ Cu ₃ (4,4'-pytz) ₃]·[N(CN) ₂]	46	19
Pt-Ni cluster/rGO	1.98	20

REFERENCES

(1) Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

- (2) Lu, T.; Chen, F. Multiwfn: A Multifunctional Wavefunction Analyzer. *J. Comput. Chem.* **2012**, *33*, 580-592.
- (3) Humphrey, W.; Dalke, A.; Schulten K., VMD: Visual Molecular Dynamics. *J. Mol. Graph.* 1996, *14*,33.
- (4) Liang, G.; Tao, L.; Tsang, Y. H.; Zeng, L.; Liu, X.; Li, J.; Qu, J.; Wen, Q., Optical Limiting Properties of A Few-Layer MoS₂/PMMA Composite under Excitation Of Ultrafast Laser Pulses. *J. Mater. Chem. C* **2019**, *7*, 495-502.
- (5) Cheng, H.; Dong, N.; Bai, T.; Song, Y.; Wang, J.; Qin, Y.; Zhang, B.; Chen, Y., Covalent Modification of MoS₂ with Poly(N-vinylcarbazole) for Solid-State Broadband Optical Limiters. *Chem. Eur. J.* **2016**, *22*, 4500-4507.
- (6) Liu, Z.; Dong, N.; Jiang, P.; Wang, K.; Wang, J.; Chen, Y., Reduced Graphene Oxide Chemically Modified with Aggregation-Induced Emission Polymer for Solid-State Optical Limiter. *Chem. Eur. J.* **2018**, *24*, 19317-19322.
- (7) Shi, M.; Huang, S.; Dong, N.; Liu, Z.; Gan, F.; Wang, J.; Chen, Y., Donor-Acceptor Type Blends Composed of Black Phosphorus and C₆₀ for Solid-State Optical Limiters. *Chem. Commun.* **2018**, *54*, 366-369.
- (8) Du, Y.; Dong, N.; Zhang, M.; Zhu, K.; Na, R.; Zhang, S.; Sun, N.; Wang, G.; Wang, J., Covalent Functionalization Of Graphene Oxide with Porphyrin and Porphyrin Incorporated Polymers for Optical Limiting. *Phy. Chem. Chem. Phy.* **2017**, *19*, 2252-2260.
- (9) Samal, M.; Valligatla, S.; Saad, N. A.; Rao, M. V.; Rao, D. N.; Sahu, R.; Biswal, B. P., A Thiazolo 5,4-D Thiazole-Bridged Porphyrin Organic Framework as A Promising Nonlinear Optical Material. *Chem. Commun.* **2019**, *55*, 11025-11028.
- (10) Biswal, B. P.; Valligatla, S.; Wang, M.; Banerjee, T.; Saad, N. A.; Mariserla, B. M. K.; Chandrasekhar, N.; Becker, D.; Addicoat, M.; Senkovska, I.; Berger, R.; Rao, D. N.; Kaskel, S.; Feng, X., Nonlinear Optical Switching in Regioregular Porphyrin Covalent Organic Frameworks. *Angew. Chem. Int. Ed.* **2019**, *58*, 6896-6900.
- (11) Liu, Z.-B.; Tian, J.-G.; Guo, Z.; Ren, D.-M.; Du, F.; Zheng, J.-Y.; Chen, Y.-S., Enhanced Optical Limiting Effects in Porphyrin-Covalently Functionalized Single-Walled Carbon Nanotubes. *Adv. Mater.* **2008**, *20*, 511-515.

- (12) Xu, B.-W.; Niu, R.-J.; Liu, Q.; Yang, J.-Y.; Zhang, W.-H.; Young, D. J., Similarities and Differences Between Mn(II) And Zn(II) Coordination Polymers Supported by Porphyrin-Based Ligands: Synthesis, Structures and Nonlinear Optical Properties. *Dalton Trans.* **2020**, *49*, 12622-12631.
- (13) ul Hassan, S.; Nawaz, F.; Khan, Z. U. H.; Firdous, A.; Farid, M. A.; Nazir, M. S., Optical materials: Studying the Role of Heteropolyacid to Enhance The Nonlinear Optical Responses of Porphyrin in Their Hybrids System. *Opt. Mater.* **2018**, *86*, 106-112.
- (14) Niu, R.-J.; Zhou, W.-F.; Liu, Y.; Yang, J.-Y.; Zhang, W.-H.; Lang, J.-P.; Young, D. J., Morphology-Dependent Third-Order Optical Nonlinearity of A 2D Co-Based Metal-Organic Framework with A Porphyrinic Skeleton. *Chem. Commun.* **2019**, *55*, 4873-4876.
- (15) Jiang, P.; Zhang, B.; Liu, Z.; Chen, Y., MoS₂ Quantum Dots Chemically Modified with Porphyrin for Solid-State Broadband Optical Limiters. *Nanoscale* **2019**, *11*, 20449-20455.
- (16) Jia, N.; He, C.; Wang, S.; Song, W.; Chen, Z.; Zu, Y.; Gao, Y.; Dong, Y., Effect of Central Metals And Peripheral Substituents on The Third-Order Nonlinear Optical Properties of Tetra-Benzimidazole and Benzothiazole Substituted Phthalocyanines. *Opt. Mater.* **2018**, *76*, 81-89.
- (17) Matshitse, R.; Khene, S.; Nyokong, T., Photophysical and Nonlinear Optical Characteristics of Pyridyl Substituted Phthalocyanine Detonation Nanodiamond Conjugated Systems in Solution. *Diamond. Relat. Mater.* **2019**, *94*, 218-232.
- (18) Krishna, M. B. M.; Kumar, V. P.; Venkatramaiah, N.; Venkatesan, R.; Rao, D. N., Nonlinear Optical Properties of Covalently Linked Graphene-Metal Porphyrin Composite Materials. *Appl. Phys. Lett.* **2011**, *98*, 081106.
- (19) Li, J.; Jia, D.; Meng, S.; Zhang, J.; Cifuentes, M. P.; Humphrey, M. G.; Zhang, C., Tetrazine Chromophore-Based Metal-Organic Frameworks with Unusual Configurations: Synthetic, Structural, Theoretical, Fluorescent, and Nonlinear Optical Studies. *Chem. Eur. J.* **2015**, *21*, 7914-7926.

(20) Zheng, C.; Lei, L.; Huang, J.; Chen, W.; Li, W.; Wang, H.; Huang, L.; Huang, D., Facile Control of Metal Nanoparticles from Isolated Nanoparticles to Aggregated Clusters on Two-Dimensional Graphene to Form Optical Limiters. *J. Mater. Chem. C* **2017**, *5*, 11579-11589.