

## **Porphyrin-Based Metal-Organic Frameworks: Hydrogen**

### **Protonation Induced Q band Absorption**

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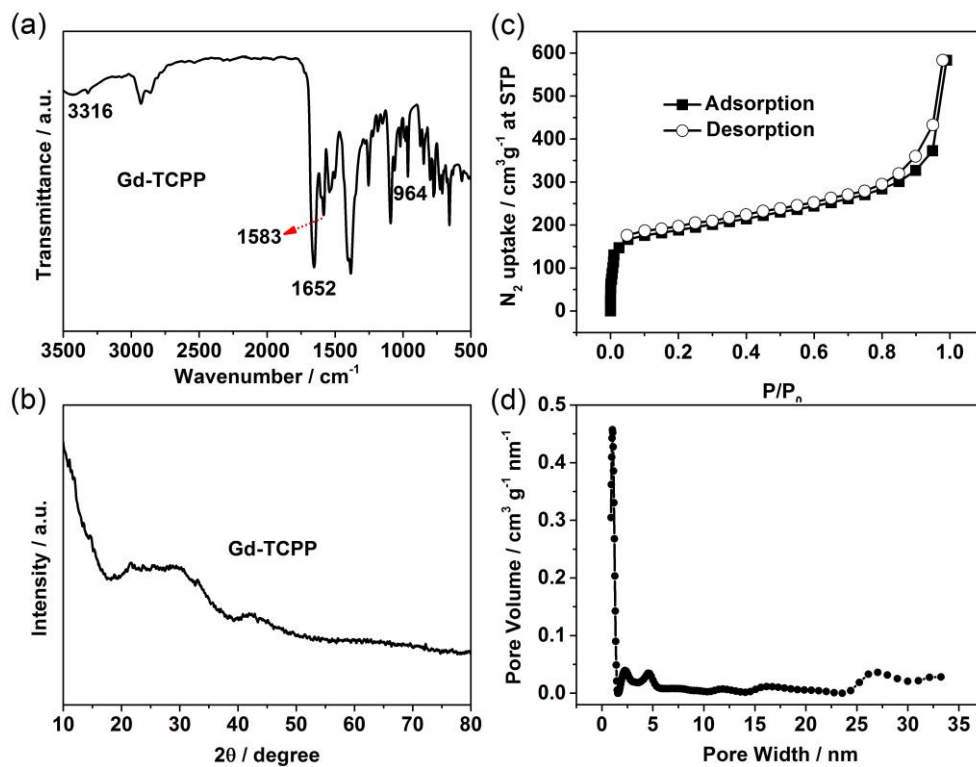
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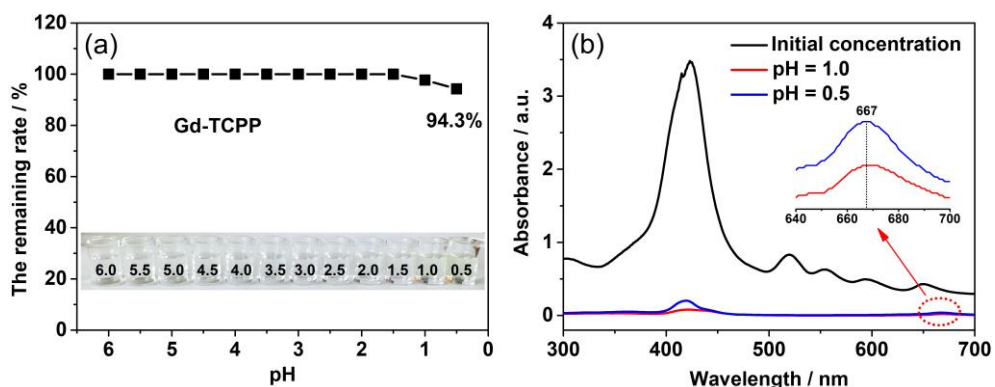
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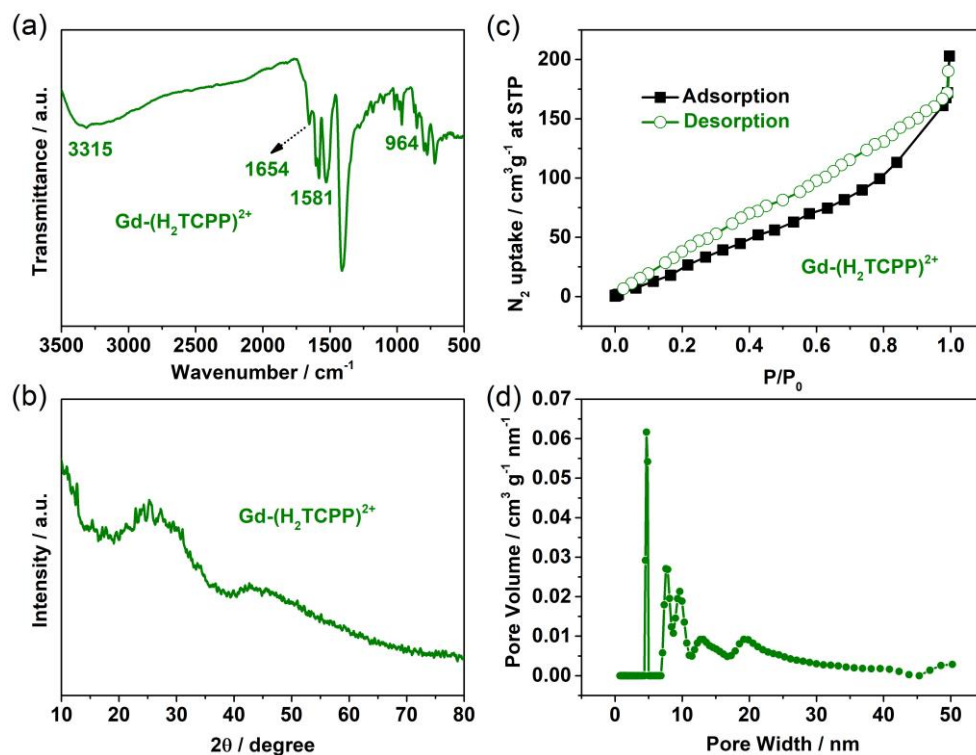
E-mail: jewang2012@sinano.ac.cn; rjpei2011@sinano.ac.cn; Tel: +86-512-62872776.



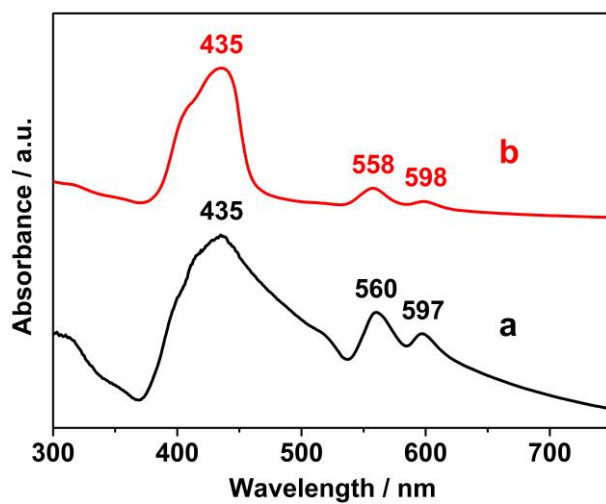
**Figure S1.** (a) FT-IR, (b) XRD, (c) N<sub>2</sub> adsorption-desorption isotherms, and (d) pore size distribution of the prepared Gd-TCPP MOFs nanosheets. The Gd-TCPP shows an approximate type I Langmuir isotherms with a Brunauer-Emmett-Teller surface area of 646.4 m<sup>2</sup> g<sup>-1</sup>.



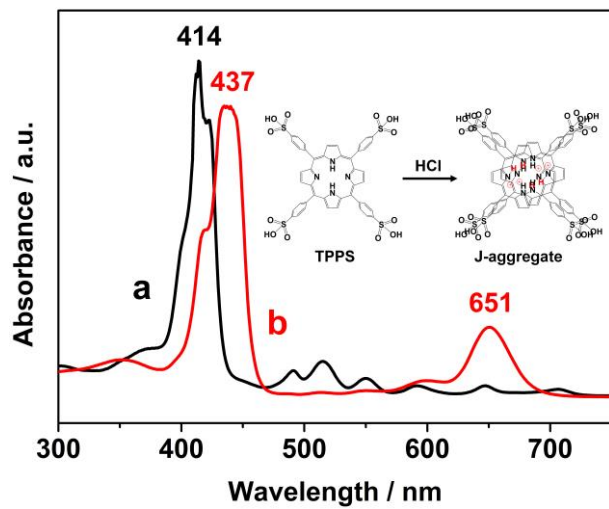
**Figure S2.** (a) Remaining rate of Gd-TCPP MOFs nanosheets obtained by hydrochloric acid treatment and centrifugation with the different pH. Inset is the photograph of supernatants obtained after hydrochloric acid treatment and centrifugation. (b) UV-vis absorption of the initial concentration of Gd-TCPP MOFs nanosheets, and UV-vis absorption of the residues in the solution after hydrochloric acid treatment and centrifugation at pH=0.5, 1.



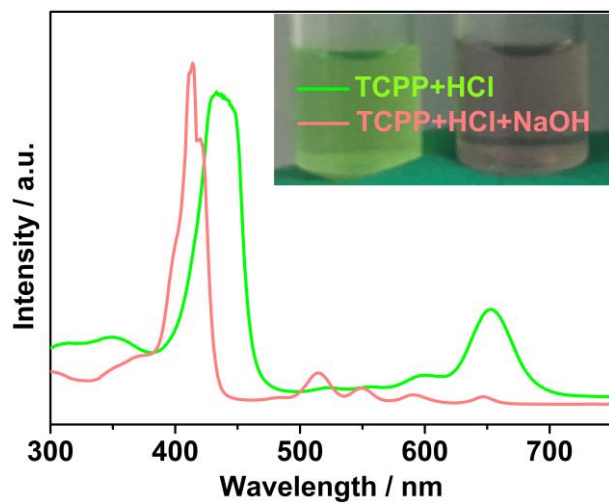
**Figure S3.** (a) FT-IR, (b) XRD, (c) N<sub>2</sub> adsorption-desorption isotherms, and (d) pore size distribution of the Gd-(H<sub>2</sub>TCPP)<sup>2+</sup>. The Gd-(H<sub>2</sub>TCPP)<sup>2+</sup> showed an approximate type II Langmuir isotherms with a Brunauer-Emmett-Teller (BET) surface area of 169.96 m<sup>2</sup> g<sup>-1</sup>.



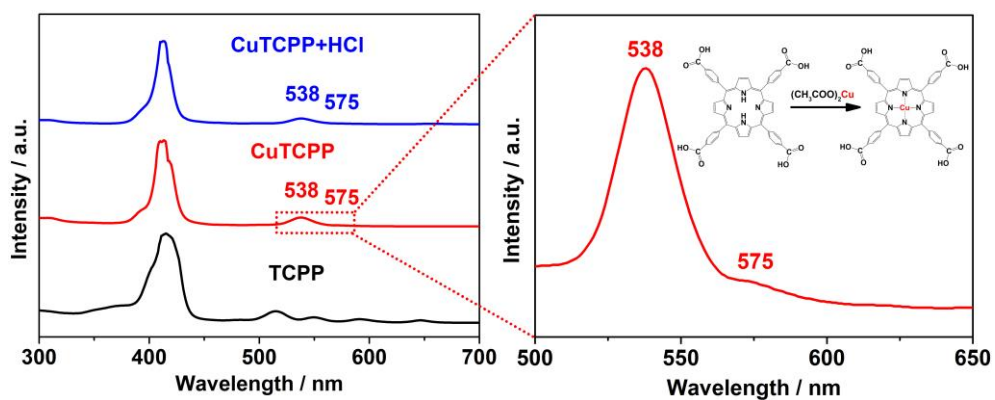
**Figure S4.** UV-vis absorption of (a) Zn-TCPP MOFs nanosheets and (b) acid-treated Zn-TCPP MOFs nanosheets.



**Figure S5.** UV-vis absorption of (a) TPPS and (b) acid-treated TPPS.



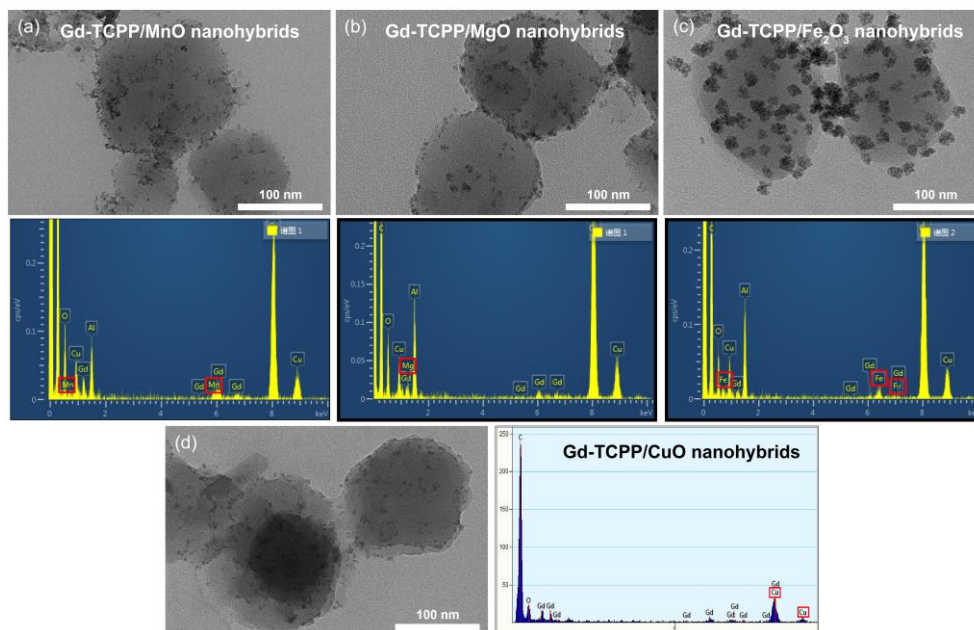
**Figure S6.** UV-vis absorption and photograph of the acid-treated and recovered TCPP.



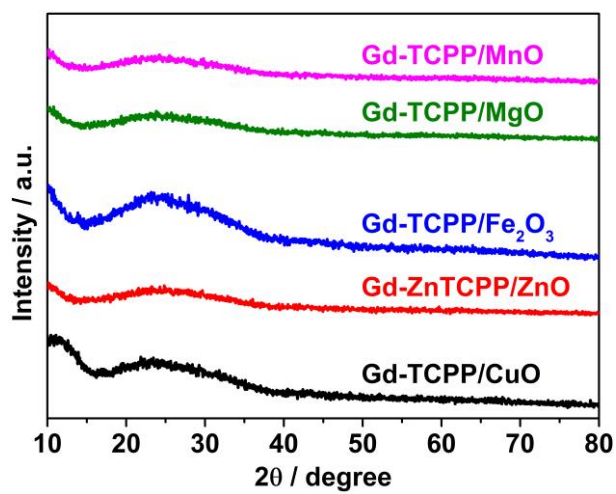
**Figure S7.** UV-vis absorption of TCP, CuTCP, and acid-treated CuTCP (pH=1.0).

The CuTCP was prepared by reacting TCP with copper acetate.





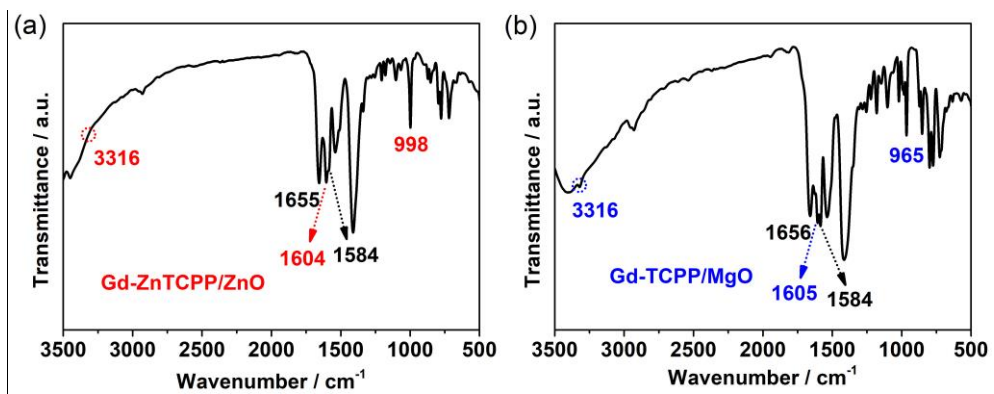
**Figure S8.** TEM and EDS images of (a) Gd-TCPP/MnO, (b) Gd-TCPP/MgO, (c) Gd-TCPP/Fe<sub>2</sub>O<sub>3</sub>, and (d) Gd-TCPP/CuO nanohybrids.



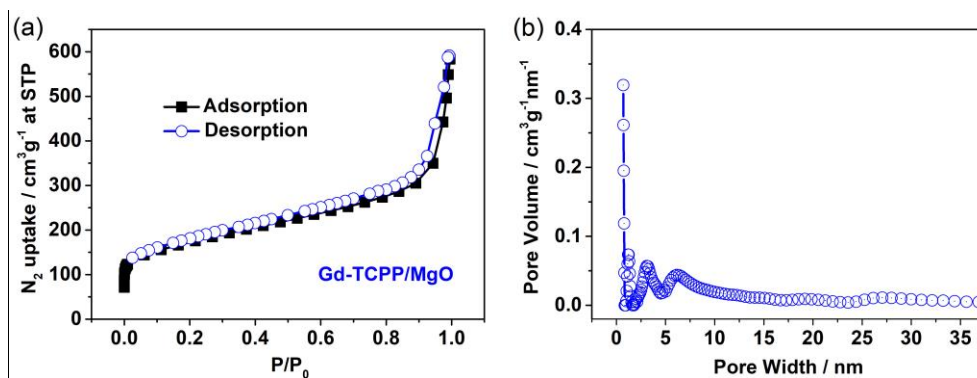
**Figure S9.** XRD patterns of the Gd-TCPP/MnO, Gd-TCPP/MgO, Gd-TCPP/Fe<sub>2</sub>O<sub>3</sub>, Gd-ZnTCPP/ZnO, and Gd-TCPP/CuO nanohybrids.



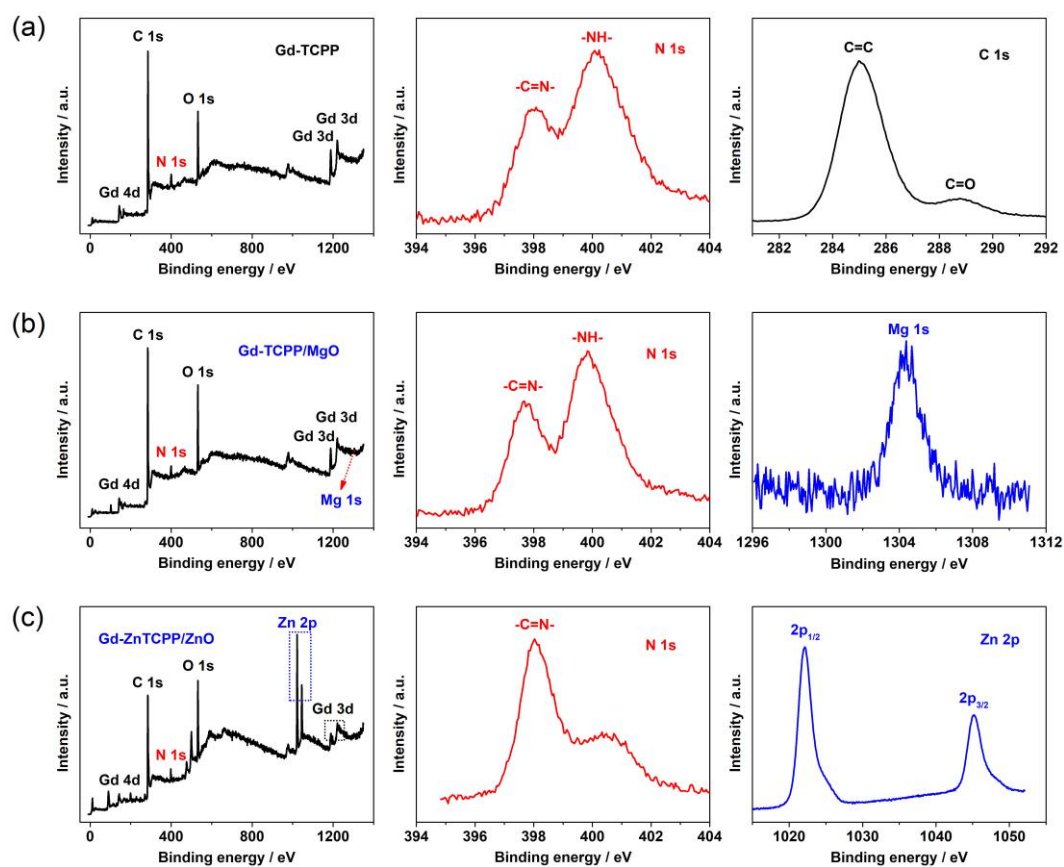
**Figure S10.** Tyndall effect has been observed for the Gd-TCPP, Gd-TCPP/CuO, Gd-ZnTCPP/ZnO, Gd-TCPP/Fe<sub>2</sub>O<sub>3</sub>, Gd-TCPP/MgO, and Gd-TCPP/MnO nanohybrids.



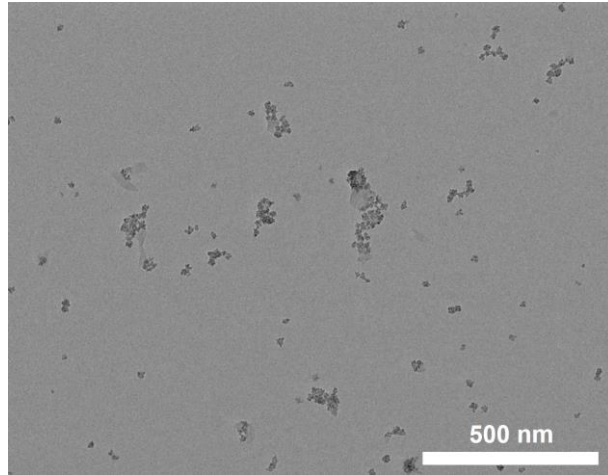
**Figure S11.** FT-IR of the (a) Gd-ZnTCPP/ZnO and (b) Gd-TCPP/MgO nanohybrids.



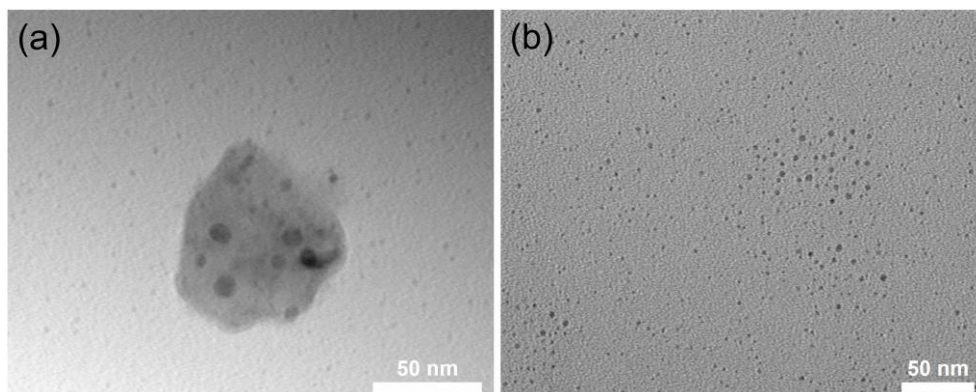
**Figure S12.** (a)  $N_2$  adsorption-desorption isotherms and (b) pore size distribution of the Gd-TCPP/MgO nanohybrids. The Gd-TCPP/MgO shows an approximate type I Langmuir isotherms with a Brunauer-Emmett-Teller surface area of  $608.6 \text{ m}^2 \text{ g}^{-1}$ .



**Figure S13.** (a) Full XPS spectrum, N 1s spectrum, and C 1s spectrum of the Gd-TCPP nanosheets. (b) Full XPS spectrum, N 1s spectrum, and Mg 1s spectrum of the Gd-TCPP/MgO nanohybrids. (c) Full XPS spectrum, N 1s spectrum, and Zn 2p spectrum of the Gd-ZnTCPP/ZnO nanohybrids.



**Figure S14.** TEM image of the acid-treated Gd-TCPP/Fe<sub>2</sub>O<sub>3</sub> nanohybrids.

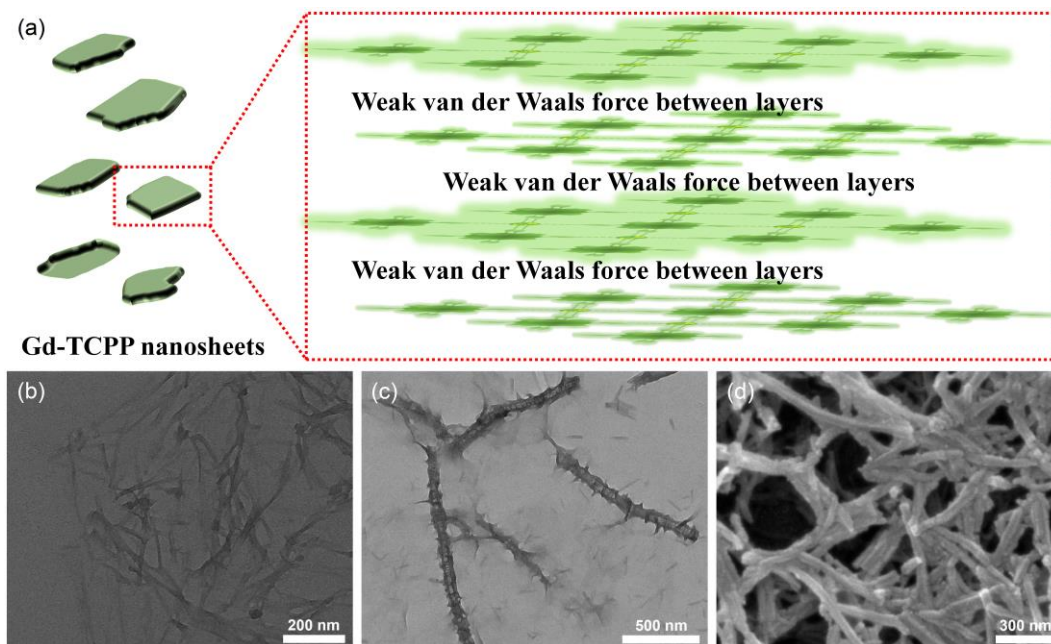


**Figure S15.** TEM images of the acid-treated Gd-ZnTCPP/ZnO nanohybrids.

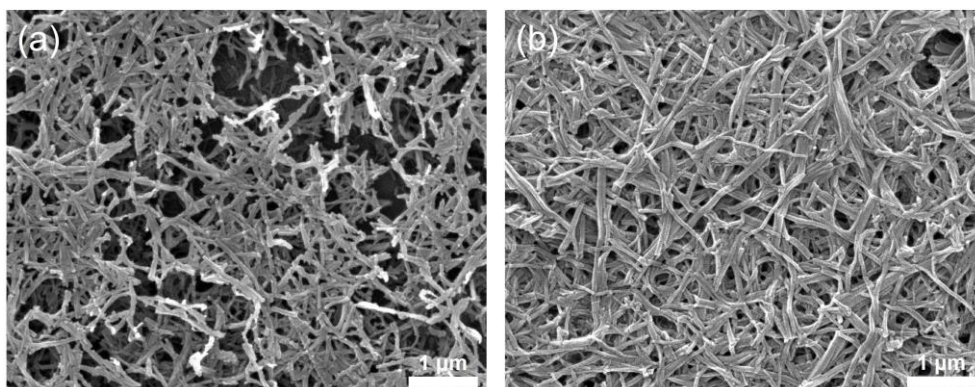


MOFs	Porphyrin	Porphyrin core	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Q-band number	Ref
COF-366-Co	Co(TAP)	Co	1360	2	S1
Co-TCPP(Fe)	TCPP(Fe)	Fe	-	2	S2
M-UiO	H <sub>2</sub> DBP-Pt	Pt	-	2	S3
Zn-TCPP(BP)	TCPP	Zn	483	2	S4
{CuL-[Al(OH) <sub>2</sub> ] <sub>2</sub> } <sub>n</sub>	H <sub>6</sub> L	Cu	-	2	S5
Ru-TBP-Zn	H <sub>4</sub> TBP	Zn	422	2	S6
Ru-TBP	H <sub>4</sub> TBP	None	441	4	S6
DBP-UiO	H <sub>2</sub> DBP	None	558	4	S7
PCN-222	H <sub>2</sub> TCPP	None	1728	4	S8
Gd-TCPP	TCPP	None	646.4	4	This work
Gd-TCPP/MgO	TCPP	None	608.6	4	This work
Gd-(H <sub>2</sub> TCPP) <sup>2+</sup>	TCPP	H	169.96	1	This work

**Table S1.** Summary of the different porphyrin-based MOFs materials.



**Figure S16.** (a) Schematic diagram of the layered Gd-TCPP nanosheets. (b, c) TEM and (d) SEM images of the acid-treated Gd-TCPP nanosheets.



**Figure S17.** SEM images of the Gd-TCPP with the acid-treated at (a) pH=3.0 and (b) pH=0.5.

## References

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