Supplementary Information

Bottom-Up Fabrication of Semiconducting 2D Coordination Nanosheets for Versatile Bioimaging and Photodetecting Applications

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1 Materials

4-bromonitrile, 4-Formylphenylboronic acid, acetyl pyridine, Potassium carbonate (K_2CO_3), and Tetrakis(triphenylphosphine)palladium (0) ($Pd(PPh_3)_4$) were purchased from Dongguan and Aladdin Chemical Reagent Co., Ltd., respectively, and used without further purification. 1,4-Dioxane, aqueous Ammonia 28 % and common solvents of analytical grade were supplied by AR Chemical Co. Ltd. 3-(4, 5-dimethyl-thiazol-2-yl)-2,5-diphenyl tetrazolium bromide (MTT) was acquired from Macklin. Dulbecco's modified Eagle's medium (DMEM), fatal bovine serum (FBS), Antibiotic and Antimycotic solution and Dulbecco's Phosphate Buffered Saline (DPBS) were procured from Gibco.

1.1 Ligand synthesis

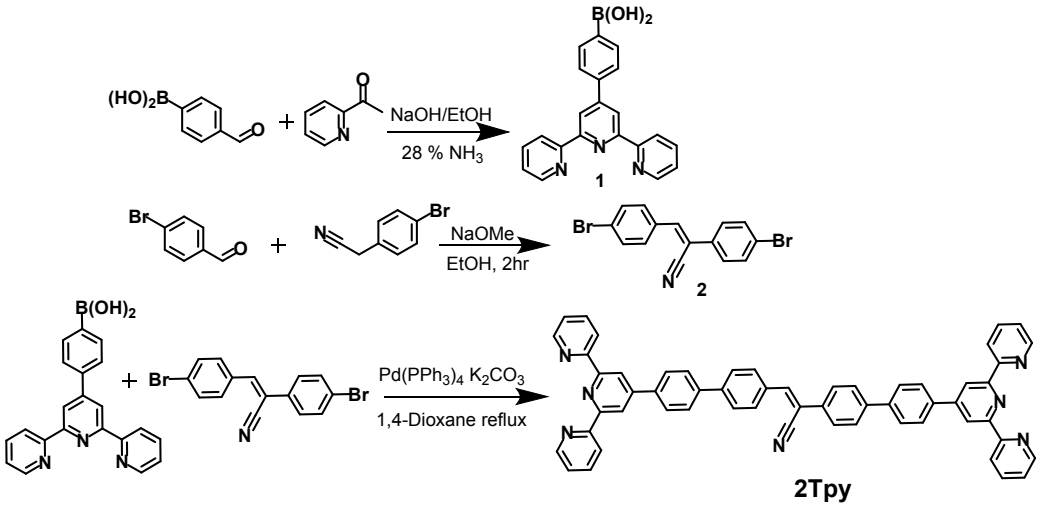
Ligand was synthesized by three-step reactions as shown in **Scheme S1**. **1** and **2** monomers were synthesized according to the previous reports [S1, 2].

1.2 Synthesis of 2Tpy:

Compound **1** (778 mg, 2.20 mmol) and compound **2** (400 mg, 1.10 mmol) in 1,4-Dioxane/H_2O (14 ml/2 ml) was added in a two-neck flask. The mixture was purged with N_2 for 3 times. Subsequently, K_2CO_3 (1216 mg, 8.8 mmol) and $Pd(PPh_3)_4$ (15 mol %) were added. The reaction mixture was stirred at 100 ^oC for 24 h. After cooling to room temperature the precipitate was filtered off followed by washing with chloroform, DMF and water, to give green solid product in 60 % yield.

^1H NMR (600 MHz, TFA) δ 9.23 (d, J = 5.7 Hz, 4H), 9.04 (d, J = 8.2 Hz, 4H), 8.97 – 8.93 (m, 8H), 8.33 (t, J = 6.8 Hz, 4H), 8.14 (d, J = 8.1 Hz, 2H), 8.11 – 8.02 (m, 8H), 7.99 (s, 1H), 7.98 – 7.89 (m, 6H).

MALDI-TOF-MS: Cacld for $[M + H]^+$: 820.31; found: 820.37.



Scheme S1 Synthetic route of 2Tpy ligand.

Compound 1:

^{1}H NMR (600 MHz, Methanol-d_4) δ 8.73 (ddd, J = 4.8, 1.8, 0.9 Hz, 2H), 8.70 (s, 2H), 8.68 (d, J = 8.0 Hz, 2H), 8.03 (td, J = 7.7, 1.8 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.1 Hz, 2H), 7.51 (ddd, J = 7.5, 4.8, 1.2 Hz, 2H).

Compound 2:

^{1}H NMR (600 MHz, Chloroform-d) δ 7.78 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H), 7.61 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H), 7.48 (s, 1H).

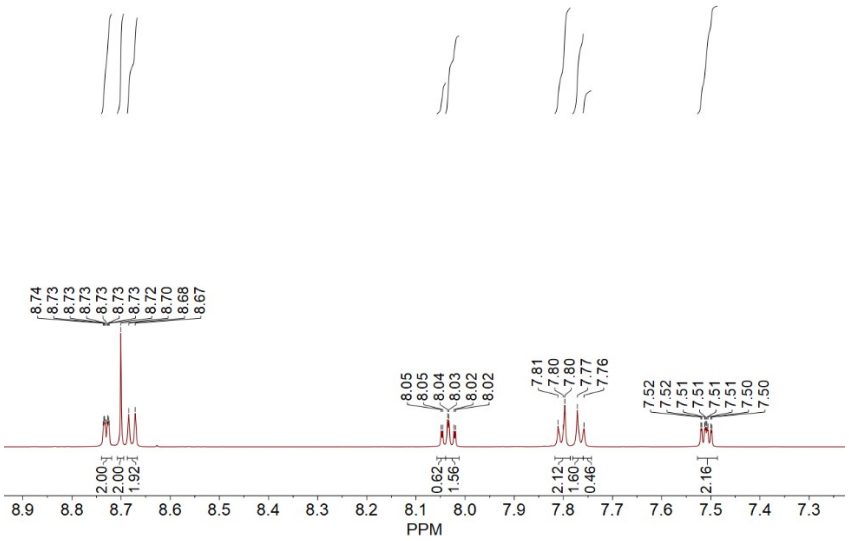


Fig. S1 [1]H NMR of compound **1**.

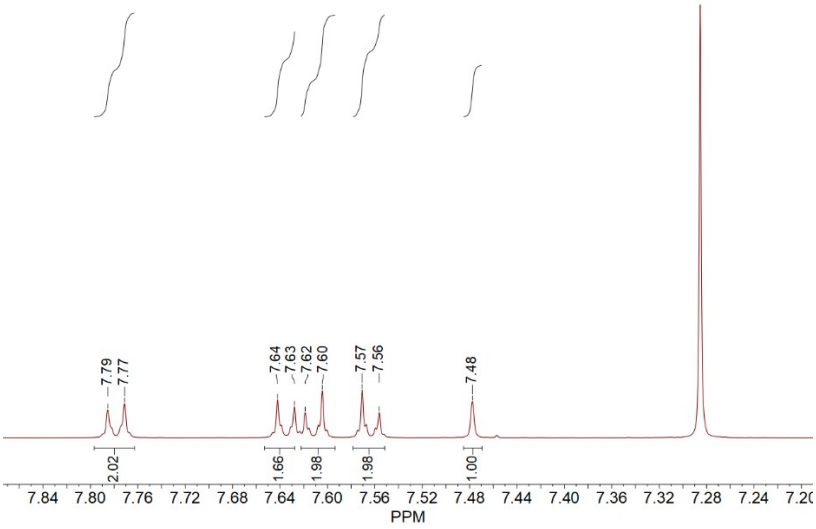


Fig. S2 [1]H NMR of compound **2**.

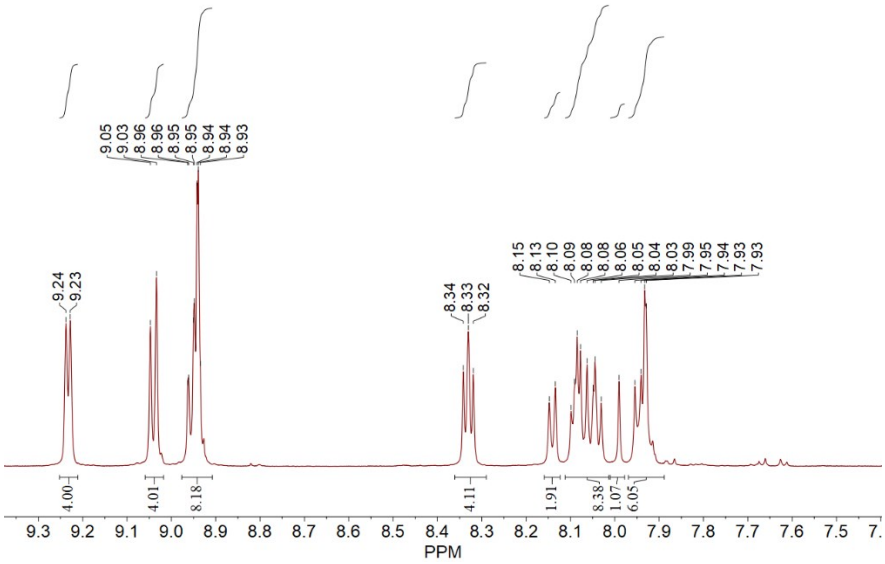


Fig. S3 ^{1}H NMR of compound 2Tpy.

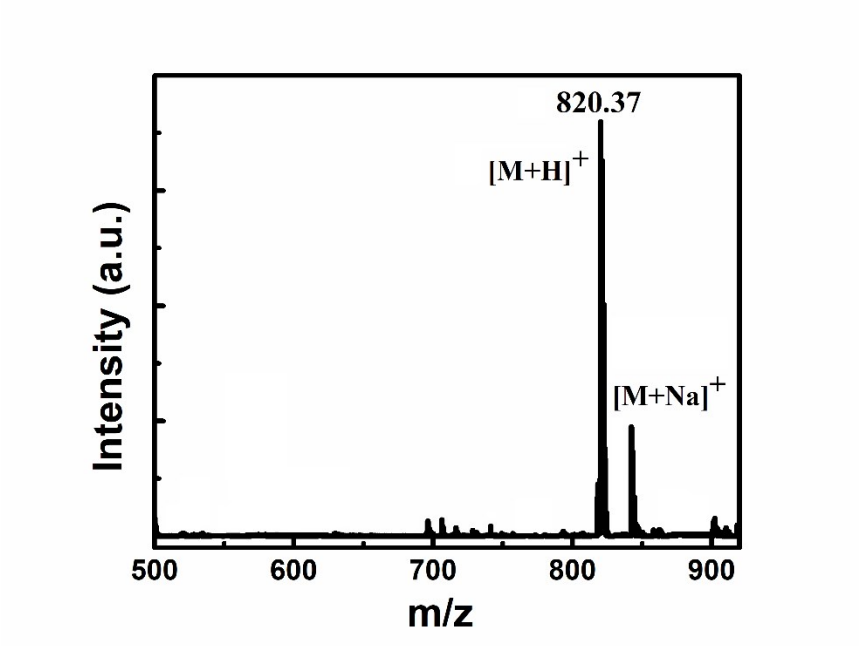


Fig. S4 MALDI-TOF-MS of 2Tpy ligand.

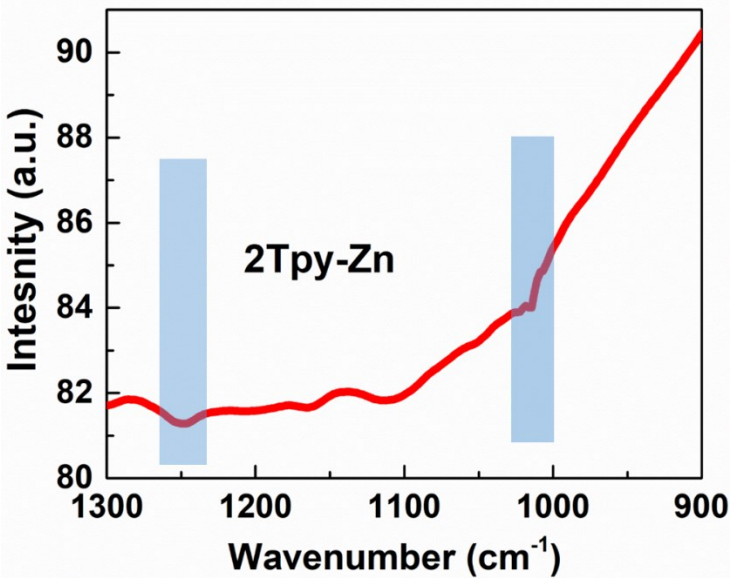


Fig. S5 IR spectrum of 2Tpy-Zn.

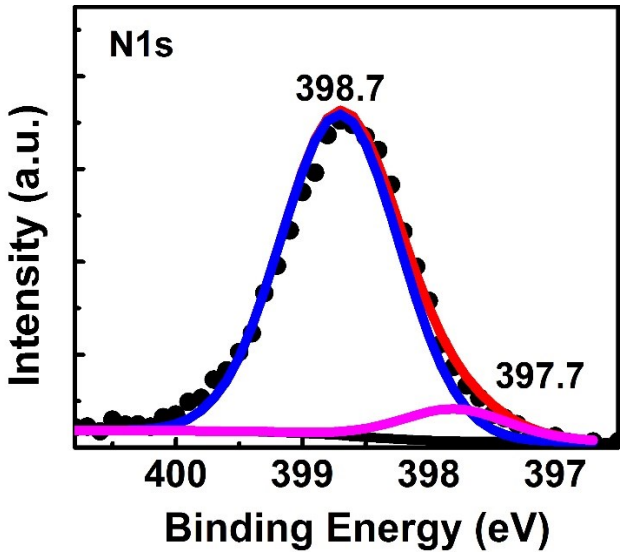


Fig. S6 N1s XPS spectrum of 2Tpy.

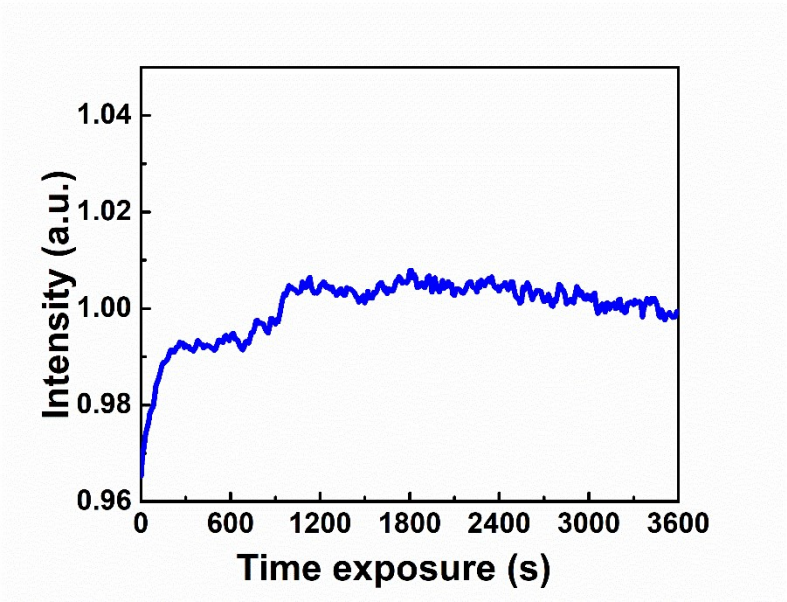


Fig. S7 PL intensity of 2Tpy-Zn CONASH NP aqueous suspension measured at a time interval of 0.5 s.

2 Cell culture and cytotoxicity assay

The 4T1 cells were cultured in Dulbecco's modified Eagle's medium (DMEM, Gibco^{TM}) containing 10% Fetal Bovine Serum (FBS, Gibco^{TM}), 1% Antibiotic and Antimycotic solution (Gibco^{TM}) at 37 °C in a humidified atmosphere with 5% CO_2, and all the cells were attached on the bottom of the 55 mm dish. In the logarithmic phase of cell growth, the 4T1 cells were harvested with Trypsin-EDTA solution (Gibco^{TM}) and dispersed in the fresh culture medium for later use.

The cytotoxicity of 2Tpy-Zn was evaluated by the MTT assay. The 4T1 cells (90 μL) were sowed on 96-well plate in which the density was about 1×10^4 cells per well. And 90 μL pure culture medium in each well was set as a blank. The cells were then cultivated at 37 °C in a humidified atmosphere with 5% CO_2 for 24 h. When the cells were completely attached, the 2Tpy-Zn suspension with different concentrations were added to the cells for 10 μL per well, and the final concentrations of 2Tpy-Zn in cells were 12.5, 25, 50, 100 and 200 μg mL^{-1}, respectively.

Non-treated cells were used as a control. After culturing the cells in the incubator for another 24 hours, 10 μL (5 mg mL^{-1}) MTT was introduced into the well. The cells were incubated for another 4 h. Finally, the culture medium in every well was removed carefully and 100 μL DMSO was added followed by shaking for 10 min. The absorbance of each well was measured at 570 nm using a microplate reader (Thermo Scientific Multiskan FC). The cell viability was determined using the formula:

$$C_v = ((A_t - \bar{A}_b)/(\bar{A}_C - \bar{A}_b)) \times 100\% \quad (1)$$

where C_v is the cell viability; A_t is the absorbance value of the treatment group; $\bar{A}_C$ is the average absorbance value of the control group; $\bar{A}_b$ is the average absorbance value of the blank group.

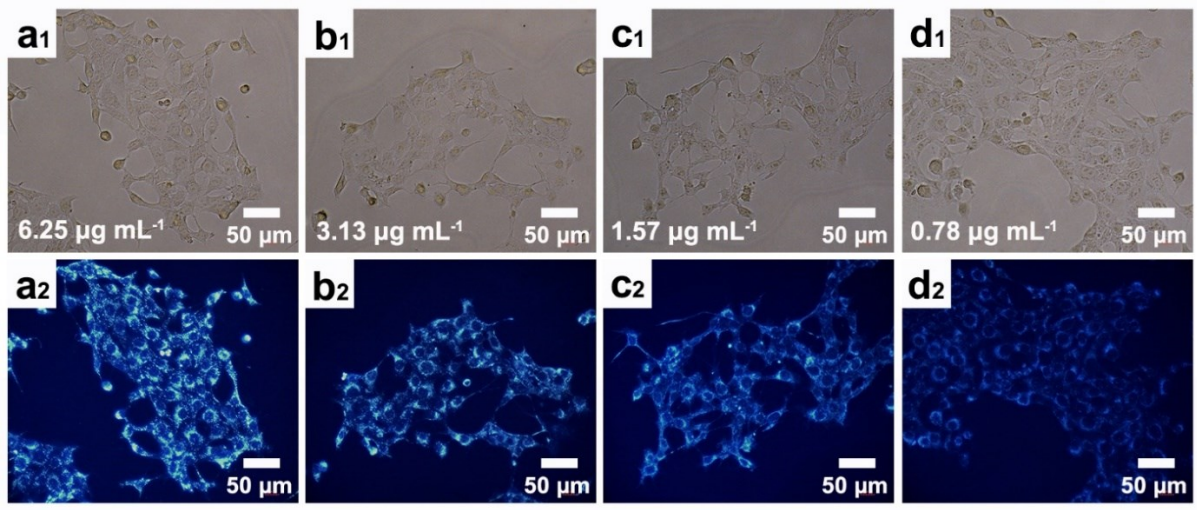


Fig. S8 a_1-d_1) Bright-field microscopic images of 4T1 cells cultured with different concentrations of 2Tpy-Zn NPs. a_2-d_2) Corresponding fluorescence microscopy images (λ_{Ex} = 350 nm).

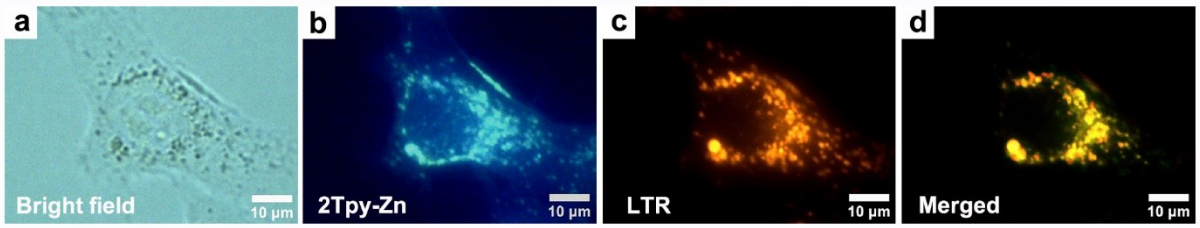


Fig S9. Co-localization imaging of 4T1 cells incubated with 2Tpy-Zn NPs and 70 nM Lyso-Tracker Red. a) Microscopic image of 4T1 cells in bright field. b) Fluorescence microscopic images of 2Tpy-Zn (λ_{Ex} = 350 nm). c) Fluorescence microscopic images of Lyso-Tracker (λ_{Ex} = 540 nm). d) Merged image of b) and c).

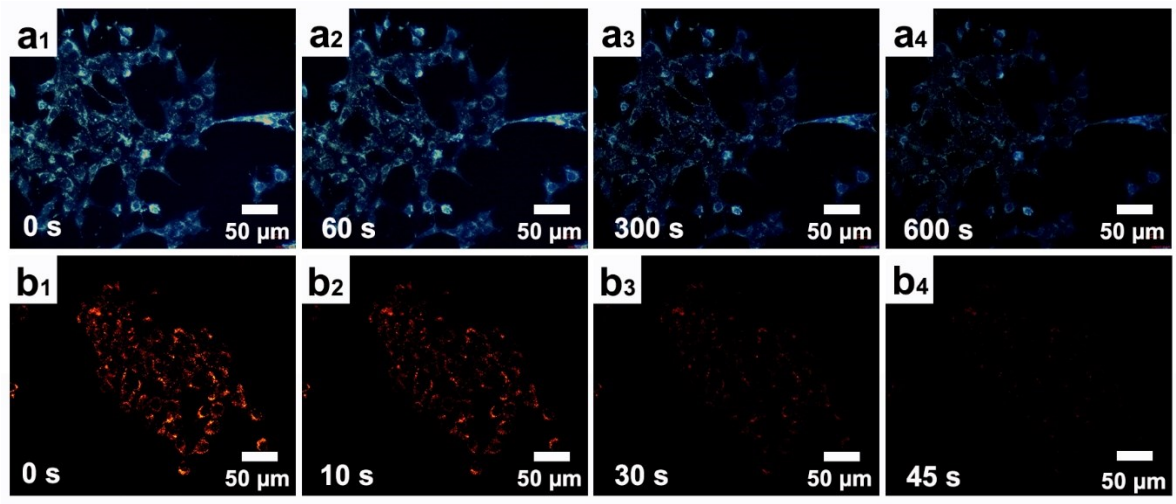


Fig. S10 a_1-a_4) Fluorescence microscopic images of 2Tpy-Zn NPs incubated 4T1 cells with different irradiation time (λ_{Ex} = 350 nm, P = 150 W). b_1-b_4) Fluorescence microscopic images of Lyso-Tracker labeled 4T1 cells with different irradiation time (λ_{Ex} = 540 nm, P = 150 W).

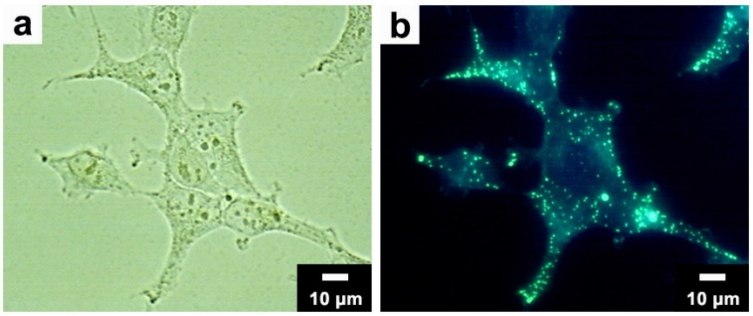


Fig. S11 Live cell imaging in normal cells (HEK 293T). a) Bright-field microscopic image. b) Fluorescence microscopic image

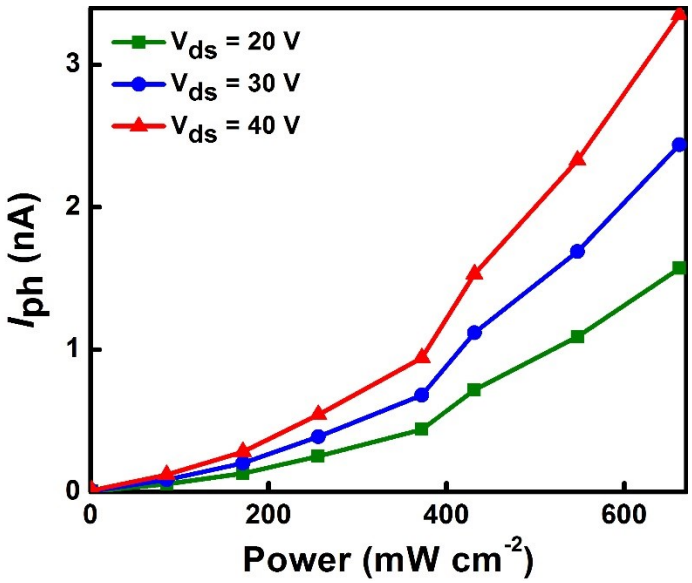


Fig. S12 Photocurrent as a function of power density at various V_{ds} under the irradiation of 450 nm.

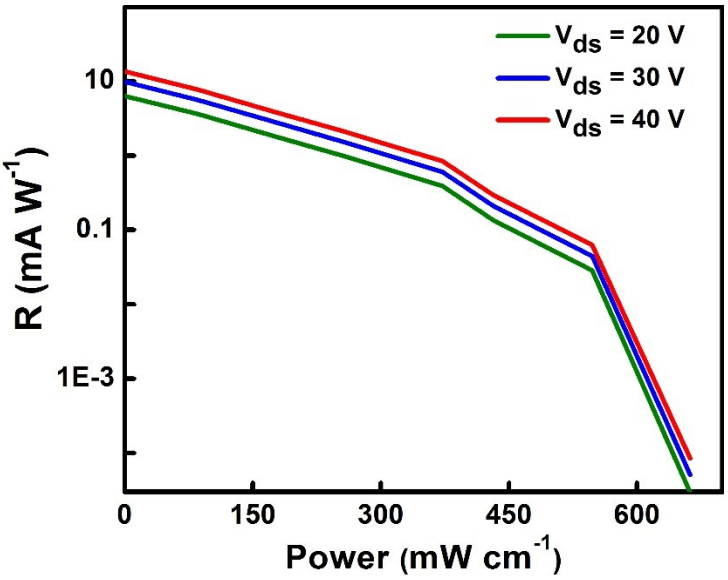


Fig. S13 Responsitivity performance at different V_{ds} under the irradiation of 450 nm.

Table S1 Summary of photodetecting properties and the comparisons with the reported MOF-, COF- and related material based photodetectors.

Materials	Responsivity	Detectivity	Rise & fall time	Ref
MOF	300 m A W^{-1}	3.2 × 10^{11} Jones	7 & 30 ms	[S3]
MOF	4 mA W^{-1} (300k)	7 × 10^{8} Jones	2.3 & 2.15 s (77K)	[S4]
MOF/Graphene	1.25 × 10^{6} AW^{-1}	6.9 × 10^{14} Jones	150 ms	[S5]
COF/graphene	3.2 × 10^{7} A W^{-1}	6×10^{13} Jones	1.14 & 4.51 ms	[S6]
2D CP	0.119 mA W^{-1}	1.29 × 10^{11} Jones	0.94 & 0.045 s	[S7]
2D 2Tpy-Zn CONASH	**13 mA W^{-1}**	**6.09 × 10^{11} Jones**	**0.072 & 0.062 s**	**This work**

Abbriviations: MOF= Metal-Organic Framewroks, COF= Covelent Organic Frameworks, CP=Coordination Polymer

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