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Supplementary Materials

Iodized BODIPY dyes as long wavelength sensitizers for near-infrared emission of ytterbium (III) ion

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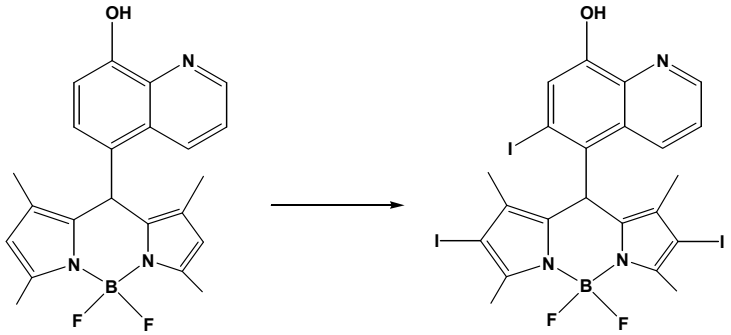
General

All solvents were treated by standard methods prior to use. Reagent grade 8-hydroxy-5-quinolinecarboxaldehyde was purchased from Leadgen Labs and used with further purification. All other chemicals were from Acros and used directly. Other chemicals were analytical grade and used as received. Elemental compositions were determined using a commercial C, H, and N analyzer. The 8-HOQ-BODIPY (**1**) was prepared as we described previously.[1]

1. Synthesis of 8-HOQ-BODIPY-3I (2).

To an ethanol solution of 8-HOQ-BODIPY (86 mg, 0.218 mmol) was added iodide (139 mg, 0.55 mmol). Then HIO_3 (77 mg, 0.44 mmol) in ethanol (20 ml) was added slowly during 10 minutes. The resulting solution was then stirred magnetically for 3h at 60˚C. The solvent was then removed and the re-dissolved in chloroform (2 mL). The solution was loaded on silica gel column and eluted with chloroform. The second band was collected. Yield: 120 mg, 72%. Anal Calcd (Found) for $C_{22}H_{17}BF_2I_3N_3O\cdot H_2O$: C, 33.58 (33.22); H, 2.42 (1.80); N, 5.34 (5.50). The ^{1}H NMR spectrum is shown in **Fig. S1**.



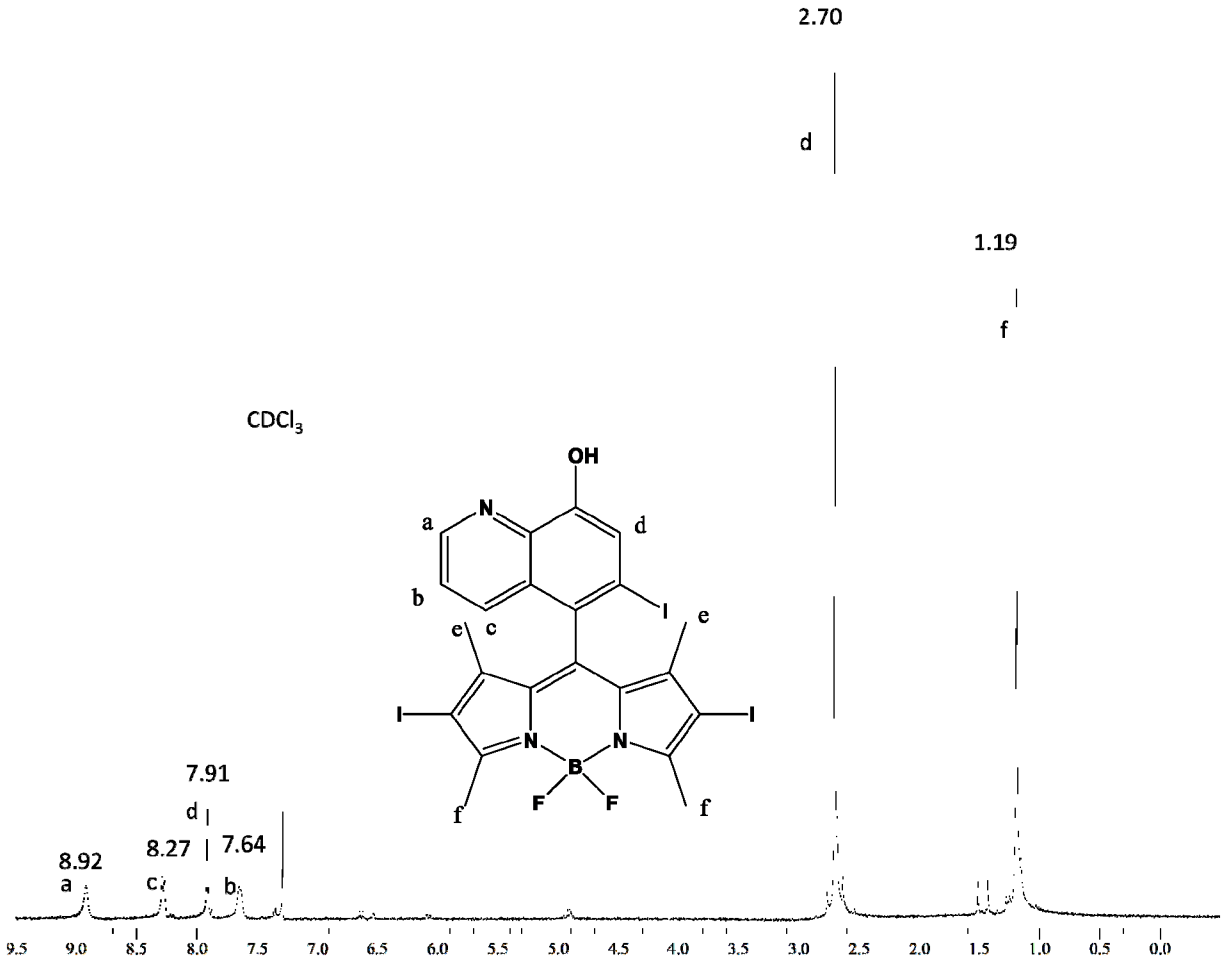


Fig. S1 ^{1}H NMR of 8-HOQ-BODIPY-3I in $CDCl_3$ (in ppm).

2. Synthesis of [Yb(8-OQ-BODIPY-3I)$_3$.H$_2$O]

To ethanol (25 mL) solution of ligand (40 mg, 0.052 mmol) was added KOH (3.5 mg, 0.04 mmol) in ethanol (2 mL), the solution became dark purple, then ytterbium (III) triflate (12 mg, 0.02 mmol) in ethanol (5 mL) was added. Golden color solid precipitated from the solution after 1h. Yield: 38 mg, 88%. Anal Calcd (Found) for $C_{66}H_{48}B_3F_6I_9N_9O_3Yb\cdot H_2O$: C, 31.77 (31.17); H, 2.02 (1.86); N, 5.05 (5.01).

3. FT-IR spectra

The FT-IR spectra were performed on a Nicolet 6700 spectrometer with KBr pellets. The ligand exhibited strong OH vibration peak at 3344 cm^{-1}. Three C-H vibration peaks were

observed at 3054, 2967, and 2921 cm^{-1}. The B-F vibration was observed at 1525 cm^{-1}. After forming complex, the OH vibration disappeared; instead a broad peak centered at 3450 cm^{-1} was observed, which was ascribed to the presence of H_2O. The presence of water was also confirmed by elemental analysis.

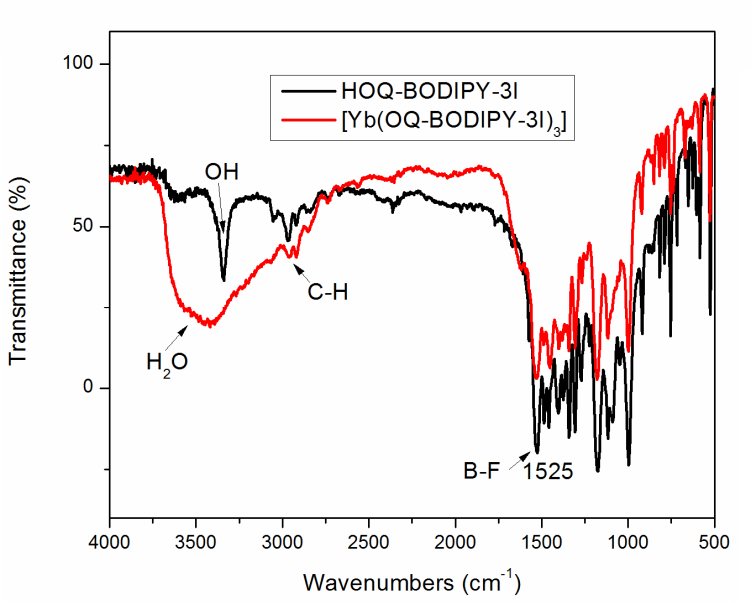


Fig. S2 FT-IR spectra of 8-HOQ-BODIPY-3I and [Yb(OQ-BODIPY-3I)$_3$.H_2O].

4. Photophysical measurements

Absorption spectra were obtained on an HP Agilent 8543 UV-visible spectrophotometer in CH_2Cl_2 at room temperature. The steady state fluorescence spectra were obtained on FS920 fluorimeter (Edinburg Instrument, Inc) with Xenon arc lamp as light source. The decay curves of the samples were measured on LifeSpec II (Edinburg Instrument, Inc.) with time-correlated single photon counting. The laser diode EPL 375 (Edinburg Instrument, Inc) with wavelength at 375 nm was used as light source. The pulse repetition frequency was 20MHz. The lifetimes were obtained by exponential fitting of deconvoluted decay data.

The quantum yield in the visible region was measured using following equation:

$$\Phi X = \left[\frac{Grad_X}{Grad_{ST}}\right]\left[\frac{n_X}{n_{ST}}\right]^2$$

where Φ is the fluorescence quantum yield, Grad the gradient from the plot of integrated fluorescence intensity vs absorbance of five samples with different concentrations, and n the

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refractive index of the solvents. The Rhodamine 6G in ethanol (Φ = 0.95, λ_{ex} = 480 nm) was used as a reference.[2] The decay curves of the samples were measured on a LifeSpec II (Edinburg Instrument, Inc.) spectrometer. The laser diode EPL 375 (Edinburg Instrument, Inc) with wavelength at 375 nm was used as light source. The lifetimes were obtained by exponential fitting of deconvoluted decay data and tail fitting of data for visible and NIR emission respectively. The rate constants of fluorescence (k_f) that are calculated from $k_f = \phi/\tau$, where ϕ is the fluorescence efficiency and τ is the decay lifetime.

Table S1 Photophysical properties of 8-HOQ-BODIPY-3I (**2**) in different solvents.

Solvents	λ_{Abs} (nm, $\varepsilon/M^{-1}\cdot cm^{-1}$)	λ_{em} (nm)	Φ_F	τ (ns)	Φ_{ISC}
$CHCl_3$	544 (8.8×10^4)	559	0.0096	0.25	0.99
CH_2Cl_2	543 (7.6×10^5)	559	0.0075	0.21	0.99
CH_3CN	537 (7.1×10^4)	556	0.0053	0.13	0.99
THF	540 (8.8×10^4)	558	0.0059	0.17	0.99
EtOH	539 (8.9×10^4)	558	0.0037	0.12	0.99
MeOH	538 (6.7×10^4)	556	0.0026	0.10	0.99

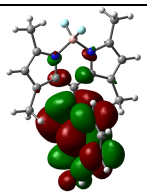
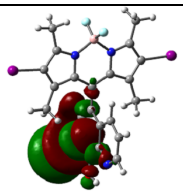
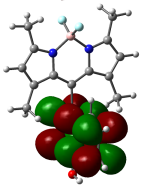
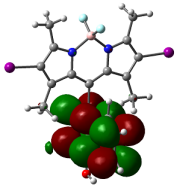
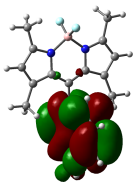
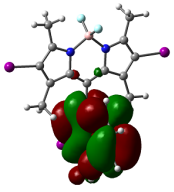
5. Theoretical calculations

Density functional theory (DFT) level calculations for geometry optimization of lanthanide complexes were carried out in vacuum on a PC using DMOl[3] implemented in Material Studio 4.3.[3] The initial structure was built with MS Visualizer. The general gradient approximation (GGA) method with the Perdew–Burke–Ernzerhof correlation (PBE) functional and double numerical plus polarization (DNP) basis were used. The treatment of core electrons includes all electrons and some relativistic effects. The calculation starts from coarse, to medium and to fine level with initial structure from lower level. The accuracy of the method for structure predication was validated by comparing bond lengths with single-crystal structure of similar lanthanide complexes as previously described.[4]

The DFT and TD-DFT calculation for the 8-HOQ-BODIPY (1) and 8-HOQ-BODIPY-3I were performed at density functional theory (DFT) level using Gaussian 09 software.[5] The initial input structures were built using structure builder tools. The ground state geometry was optimized using B3LYP functional with 6-31g(d) basis set for C, N, O, F, B and LANL2DZ for I atom. All other parameters were default set and no solvent effect was applied. No negative frequency was found in the final optimized structures. For TD-DFT calculations, a continuum (CPCM) model was used for mimicking the solvent acetonitrile.

Calculations showed that HOMO and LUMO of the 8-HOQ-BODIPY (**1**) and 8-HOQ-BODIPY-3I (**2**) located in the BODIPY units. After iodization, the energy gap between HOMO and LUMO decreased, which is reflected in a longer absorption wavelength maximum for 8-HOQ-BODIPY-3I from TD-DFT calculation. The calculated triplet state energy levels are 817.07 and 835.67 nm for 8-HOQ-BODIPY (**1**) and 8-HOQ-BODIPY-3I (**2**), respectively. Both are higher than the emitting level of Yb^{3+} ion, which are critical for the sensitization process.

Table S2 Electron density distributions of frontier molecular orbitals of 8-HOQ-BODIPY (**1**) and 8-HOQ-BODIPY-3I (**2**).

	8-HOQ-BODIPY (1)		8-HOQ-BODIPY-3I (2)	
		Energy (ev)		Energy level (ev)
LUMO+3		0.012		0.039
LUMO+2		0.031		0.045
LUMO+1		0.065		0.077

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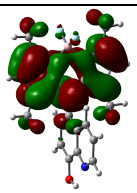
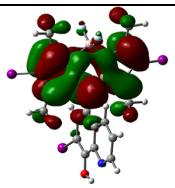
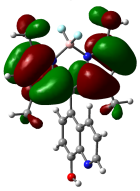
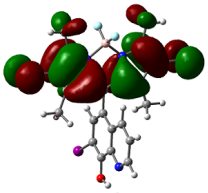
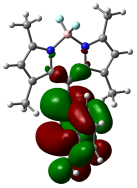
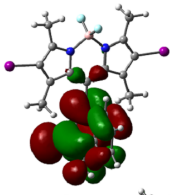
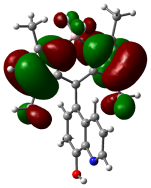
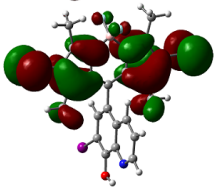
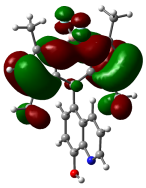
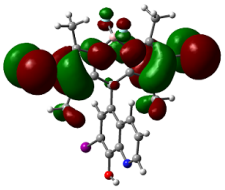
LUMO		0.089		0.107
HOMO		0.199		0.212
HOMO-1		0.221		0.230
HOMO-2		0.239		0.244
HOMO-3		0.246		0.245

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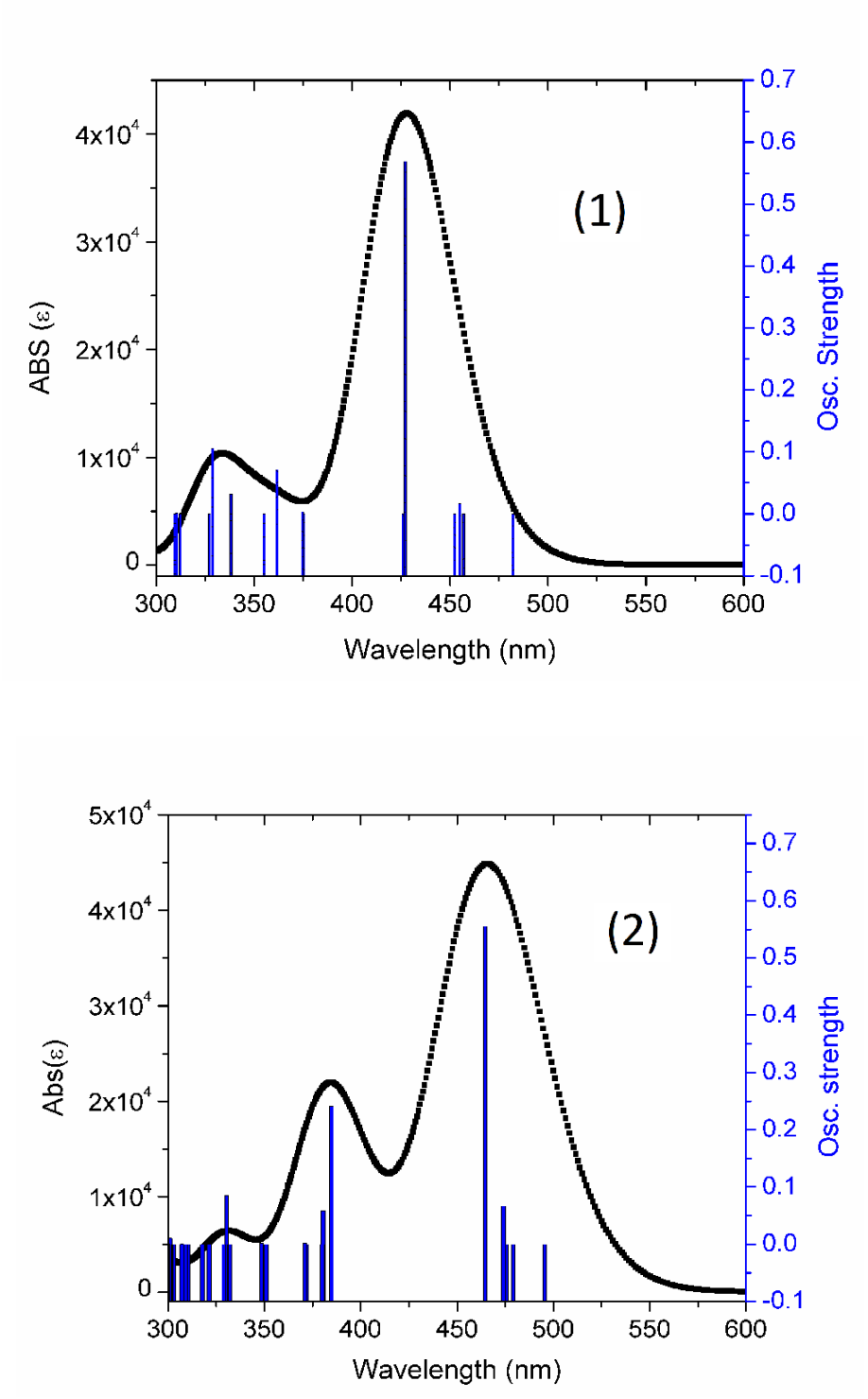

Fig. S3 Predicted absorption spectra of 8-HOQ-BODIPY (**1**) and 8-HOQ-BODIPY-3I (**2**).

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Table S3 Major transitions of two 8-HOQ-BODIPY (**1**) and 8-HOQ-BODIPY-3I (**2**) and their oscillation strength (*f*).

sensitizer	Transition (nm)	*f*	Compositions (percentage)	Character
8-HOQ-BODIPY	817.07		H → L (100%),	Triplet
	454.92	0.0166	H-1→LUMO (94%), HOMO→LUMO (6%),	Singlet
	427.14	0.5691	HOMO→LUMO (92%), H-1→LUMO (-6%),	Singlet
	361.72	0.0709	H-2→LUMO (96%), HOMO→LUMO (4%),	Singlet
	328.65	0.1057	H-1 →L+1 (96%)	Singlet
8-HOQ-BODIPY-3I	835.63		H → L (97%), H - 2 →LUMO (-5%)	Triplet
	474.15	0.0665	H-1→LUMO (85%), HOMO→LUMO (13%)	Singlet
	464.46	0.5553	H-1→LUMO (-14%), HOMO→LUMO (80%) H-2→LUMO (6%)	Singlet
	384.88	0.2418	H-2→LUMO (92%) HOMO→LUMO (-8%)	Singlet
	380.54	0.059	H-3→LUMO (99%)	Singlet
	330.45	0.0851	H-1→L+1 (95%)	Singlet

6. Atomic force microscope (AFM)

The AFM images were taken on an Agilent 5500 using noncontact mode. The AFM showed the layered structure with thickness for each layer ~ 3 nm..

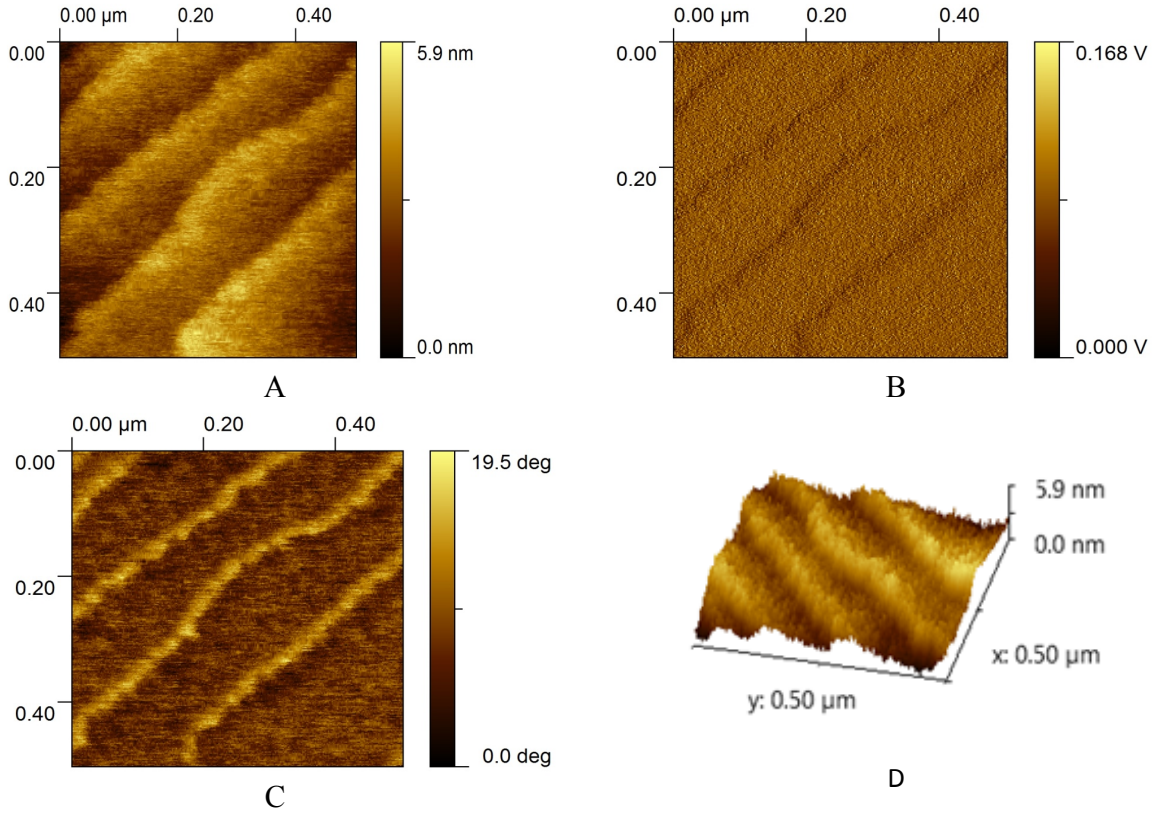

Fig. S4 The AFM images of top surface morphology of a piece of [Yb(8-OQ-BODIPY-3I)$_3$] nanosheet. A: topography; B: amplitude; C: Phase; D: topography

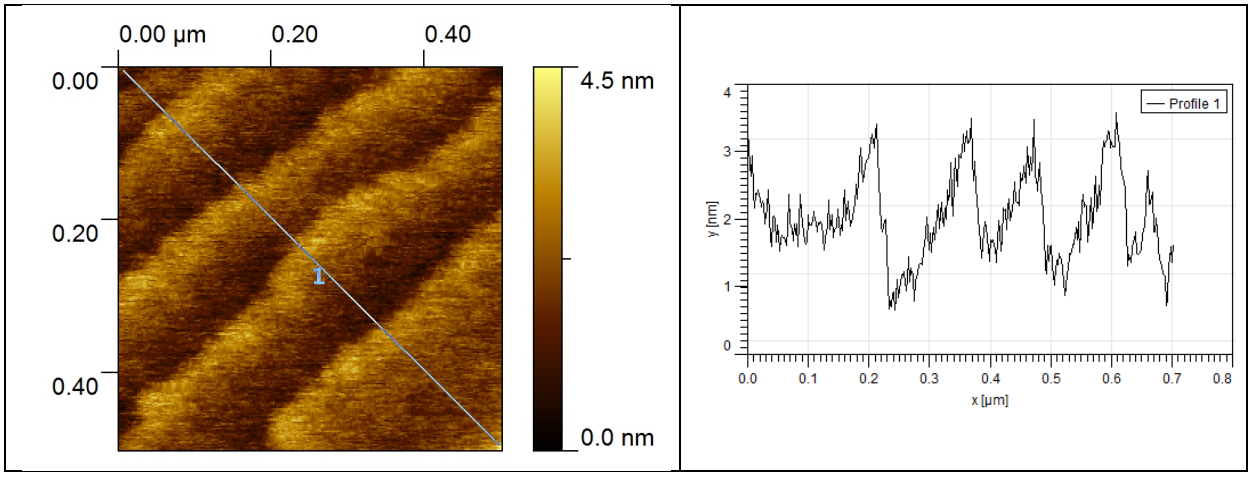

Fig. S5 Thickness profile of nanosheet of the of [Yb(8-OQ-BODIPY-3I)$_3$].

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