Electronic Supplementary Information for

A Macrocyclic 1, 4-Bis (4-pyridyl-ethynyl)benzene Showing Unique

Aggregation-Induced Emission Property

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Table of Contents

Experimental Section	S3
Scheme S1 Synthetic routes to BisPy-2Bz (M1).	S3
Scheme S2 Synthetic route to [Box][PF ₆] ₂ [Br] ₂ .	S4
Figure S1 ¹ H-NMR spectrum of BisPy (CDCl ₃ , 400 MHz).	S5
Figure S2 ¹³ C-NMR spectrum of BisPy (CDCl ₃ , 400 MHz).	S5
Figure S3 FT-IR spectrum of BisPy in KBr pellet.	S6
Figure S4 HRMS spectrum of BisPy.	S6
Figure S5 ¹ H-NMR spectrum of Box in <i>d</i> 6-DMSO.	S7
Figure S6 FT-IR spectrum of Box.	S7
Figure S7 HRMS spectrum of Box.	S8
Figure S8 UV-Vis absorption spectra of Box in DMSO/water mixtures with diff	erent
water fractions. Concentration: 10 ⁻⁵ M.	S8
Figure S9 Photoluminescence (PL) spectra (B) of Box in DMSO/water mixtures	with
different water fractions. Concentration: 10^{-5} M, λ_{ex} = 375 nm.	S9
Figure S10 Plot of the relative fluorescence intensity (I/I ₀ -1) versus water fracti	on in
DMSO/Water mixtures. Concentration: 10^{-5} M, λ_{ex} = 375 nm.	S9
Figure S11 Photoluminescence spectra of [BOX][PF ₆] ₄ in DMSO/Water systems.	S10
Figure S12 TEM images of aggregates of Box formed in DMSO/Water mixtures.	S11
Figure S13 Scanning electron microscope images of solid samples of [BOX][PF ₆].	_{1.} S11
Figure S14 FT-IR spectrum of BisPy-2Bz.	S12
Figure S15 ¹ H NMR spectrum of BisPy-2Bz.	S12
Figure S16 ¹³ C NMR spectrum of BisPy-2Bz.	S13
Figure S17 HRMS spectrum of BisPy-2Bz.	S13
Figure S18 UV-Vis absorption (A) and PL spectra (B) of BisPy-2Bz in DMSO/v	water
mixtures with different water fractions. Concentration: 10 ⁻⁵ M, λ_{ex} = 375 nm.	S14
Figure S19 Variation in the PL intensity (A) and quantum yield (B) of BisPy-2	Bz in
DMSO/Water mixtures with different water fractions.	S14
Figure S20 Variation in particle size of BisPy-2Bz in DMSO/Water mixtures	with
different water fractions. Concentration: 10 ⁻⁵ M.	S15
Figure S21 TEM image of BisPy-2Bz aggregates formed in DMSO/Water mixt	ures.
Concentration: 10 ⁻⁵ M, water fraction: 90%.	S15
Reference	S15

Experimental Section

Materials: All commercially available chemicals were purchased from J&K, Across, Alfa Aesar or Sinopharm Chemical Reagent Co., Ltd unless specially stated. These chemicals are used without further purification. THF and Et₃N were distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use.

Instrumentation: ¹H and ¹³C NMR spectra were measured on a Mercury plus 400MHz NMR spectrometer in CDCl₃ or d-DMSO using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. High-resolution mass spectra (HRMS) were taken on a GCT premier CAB048 mass spectrometer operating in a MALDI-TOF mode. Photoluminescence (PL) spectra were measured on a Perkin-Elmer LS 55 spectrofluorometer. UV-Visible absorption spectra were measured on a Varian CARY 100 Biospectrophotometer. Fluorescence quantum yields were measured using 2-aminopyridine in 0.1N H₂SO₄ (60%) for BisPy and 9,10-diphenylanthracene in cyclohexane (90%) for BisPy-2Bz and BisPy-2Et as standards. Single crystal X-ray diffraction intensity data for BisPy-2Bz and BisPy-2Et was collected on an Xcalibur, Sapphire 3, Gemini ultra-diffractometer with graphite monochromated Cu-K X-ray radiation.

Synthetic Procedures: The two compounds mentioned in the manuscript were conveniently synthesized by Sonogashira coupling and/ or nucleophilic substitution reaction between pyridyl with benzyl bromide functionalities. The synthetic routes are shown in Scheme 1 in the manuscript and Scheme S1 as below.



Scheme S1 Synthetic route to BisPy-2Bz or M1.

1,4-bis(4-pyridylethynyl)benzene (BisPy).^[1] Into a 250 mL flask was added 4-iodopyridine (2.05 g, 10 mmol), 1,4-diethynylbenzene (630 mg, 5 mmol), PdCl₂(PPh₃)₂ (0.02 mmol, 14 mg), CuI (0.04 mmol, 7.618 mg), PPh₃ (0.06 mmol, 16 mg). Then 60 mL of dried THF and 30 mL of dried Et₃N was added to the system to dissolve the mixture. The reaction mixture was then allowed to stir overnight under nitrogen at 55 °C. After the solid was filtered off, the solvent was evaporated under vacuum. The crude product was then passed through silica gel column chromatography with DCM: Acetone=10:1 as eluent to get the white powder as the product (2.46 g, 88%).

HRMS Calcd. for C₂₀H₁₂N₂: m/z = 280.1000; found: 280.1002. ¹H NMR (400 MHz, CDCl₃) δ 8.63 (d, *J* = 5.5 Hz, 4H), 7.56 (s, 4H), 7.39 (d, *J* = 5.7 Hz, 4H). ¹³C NMR (101

MHz, CDCl₃) δ 149.86 (s), 131.94 (s), 131.36 – 130.68 (m), 125.51 (s), 123.15 – 122.41 (m), 93.56 – 92.21 (m), 89.57 – 88.22 (m). IR (KBr pellet): 2221cm⁻¹ (-C=C- stretching), 1585 cm⁻¹ (-N=C- stretching).

N,N'-bisbenzyl-1,4-bis(4-pyridin-1-iumylethynyl)benzenebishexafluorophosphate (BisPy-2Bz or M1). 140 mg (0.5mmol) of BisPy was dissolved in DCM in a 100 mL two-necked flask and was then heated to reflux. 1 mL of benzyl bromide was dissolved in MeCN, and the solution was then added dropwise to the reaction system. The mixture was kept refluxing until no more precipitate can be observed to occur. The system was then cooled down. The solid was collected by filtration and then dissolved in MeOH. Saturated aqueous solution of NH_4PF_6 was added. The precipitate was collected and washed by water, MeOH, and DCM to get the product. (150 mg, 40%)

HRMS Calcd for $C_{34}H_{24}F_{12}N_2P_2$: m/z = 607.1738 [M–PF₆]⁺, 462.2096 [M–2PF₆]⁺, 371.1548 [M–2PF₆– C_7H_7]⁺; found: 607.1788 [M–PF₆]⁺, 462.1982 [M–2PF₆]⁺, 371.1686 [M–2PF₆– C_7H_7]⁺. ¹H NMR (400 MHz, DMSO) δ 9.23 (d, *J* = 6.9 Hz, 4H), 8.33 (d, *J* = 6.8 Hz, 4H), 7.87 (s, 4H), 7.55 (dd, *J* = 7.7, 1.7 Hz, 4H), 7.50–7.36 (m, 6H), 5.84 (s, 4H). ¹³C NMR (101 MHz, DMSO) δ 144.90 (s), 138.59 (s), 134.06 (s), 132.94 (s), 129.92 (s), 129.42 (s), 129.25(s), 128.82 (s), 122.15 (s), 100.91 (s), 87.81 (s), 63.21 (s). IR (KBr pellet): 2220cm⁻¹ (-C=C- stretching), 1631 cm⁻¹ (-N⁺=C- stretching).



Scheme S2 Synthetic route to [Box][PF₆]₂[Br]₂.

Cyclobis(4,4'-(1,4-phenylene)bis(4-pyridylethynyl)-p-phenylene)-tetrakis(hexafluorophosphate) (Box). 140 mg (0.5 mmol) of BisPy was dissolved in DCM in a 100 mL two-necked flask and was then heated to reflux. α, α' -Dibromo-p-xylene (1.32 g, 5 mmol) was dissolved in MeCN, and the solution was then added dropwise to the reaction system. The mixture was kept refluxing until no more precipitate can be observed to occur. The system was then cooled down. The solid was collected by filtration and then dissolved in MeOH. Saturated aqueous solution of NH₄PF₆ was added. The precipitate was collected and washed by water, MeOH, and DCM to get the product intermediate **1** (BisPy-2BzCH₂Br).

HRMS Calcd. for $C_{26}H_{38}Br_2F_{12}N_2P_2$: m/z = 793.0241 [M–PF₆]⁺, 648.0599 [M–2PF₆]⁺; found: 793.0330 [M–PF₆]⁺, 648.0397 [M–2PF₆]⁺. ¹H NMR (300 MHz, *d*-acetone) δ 9.26 (d, *J* = 6.9 Hz, 4H), 8.37 (d, *J* = 6.9 Hz, 4H), 7.85 (s, 4H), 7.67 – 7.55 (m, 8H), 6.08 (s, 4H), 4.67 (s, 4H). IR (KBr pellet) 2222cm⁻¹ (-C=C- stretching), 1631 cm⁻¹ (-N⁺=C- stretching)

Intermediate **1** (0.15 mmol, 140.25 mg), BisPy (0.15 mmol, 42 mg) and KI (0.03 mmol, 5 mg) was added into a 250 mL flask. 75 mL of MeCN was added to dissolve the mixture. The concentration of the reaction solution was 2 mM. The mixture was left to stir for 3d. The precipitate was collected and then dissolved in MeOH. Saturated aqueous solution of NH_4PF_6 was added. The precipitate was collected and washed by water, MeOH, and DCM to get the product as Box.



Figure S1 ¹H-NMR spectra of BisPy (CDCl₃, 400 MHz).



Figure S2 ¹³C-NMR spectra of BisPy (CDCl₃, 400 MHz)



Figure S3 FT-IR spectrum of BisPy in KBr pellet.



Figure S4 HRMS spectrum of BisPy.



Figure S5 ¹H-NMR spectrum of Box in *d*6-DMSO. The solvent peak is marked with asterisk.



Figure S6 FT-IR spectrum of Box in KBr pellet.



Figure S7 HRMS spectrum of Box.



Figure S8 UV-Vis absorption spectra (A) and PL spectra (B) of Box in DMSO/water mixtures with different water fractions. Concentration: 10^{-5} M.



Figure S9 Photoluminescence (PL) spectra of Box in DMSO/water mixtures with different water fractions. Concentration: 10^{-5} M, λ_{ex} = 375 nm



Figure S10 Plot of the relative fluorescence intensity (I/I_0 -1) versus water fraction (f_W) in DMSO/Water mixtures. I_0 and I are the fluorescence intensity recorded at f_W = 0 and another f_W value, respectively. Concentration: 10⁻⁵ M, λ_{ex} = 375 nm.



Figure 11 Photoluminescence (PL) spectra of [BOX][PF₆]₄ (A, B) in DMSO/Water systems. [M] = 10^{-5} M, λ_{ex} = 375 nm.

Table 1 Number /	Average Particle Sizes	of Box-like AIEgens in	DMSO/Water Mixtures ^a
	0		,

f _W (%)	Particle size (nm)
99	60
90	32
70	45
50	50

^a Particle size measured by dynamic light scattering (DLS) after the mixture solution stood still for 30 minutes. The data are just collected in one typical run.



Figure 12 TEM images of aggregates of $[BOX][PF_6]_4$ formed in DMSO/Water solvent mixtures, left image for $f_W = 90\%$ and right image for $f_W = 70\%$.



Figure 13 Scanning electron microscope images of solid samples of $[BOX][PF_6]_4$ (left: as prepared solid powder; right: solid formed in DMSO/Water solvent mixture for $f_W = 70\%$.).



Figure S14 FT-IR spectrum of BisPy-2Bz in KBr pellet.



Figure S15 ¹H-NMR spectrum of BisPy-2Bz in d_6 -DMSO. The solvent peak is marked with asterisk.



Figure S16 ¹³C-NMR spectrum of BisPy-2Bz in d-DMSO. The solvent peak is marked with asterisk.



Figure S17 HRMS spectrum of **BisPy-2Bz**.



Figure S18 UV-Vis absorption spectra (A) and PL spectra (B) of BisPy-2Bz in DMSO/water mixtures with different water fractions. Concentration: 10^{-5} M.



Figure S19 Variation in the relative PL intensity (A) and quantum yield (B) of BisPy-2Bz in DMSO/Water mixtures with different water fractions.



Figure S20 Variation in particle size of BisPy-2Bz in DMSO/Water mixtures with different water fractions. Concentration: 10^{-5} M.



Figure S21 TEM image of BisPy-2Bz aggregates formed in DMSO/water mixtures. Concentration: 10⁻⁵ M, water fraction: 90%.

Reference

^[1] P. Nguyen, Z. Yuan, L. Agocs, G. Lesley and T. B. Marder, *Inorg. Chim. Acta*, 1994, **220**, 289.