Electronic Supplementary Information (ESI)

# A Rational Designed Vapoluminescent Compound with Adsorptive Channels and Responsive Luminophores for Volatile Organic Compounds (VOCs)

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## Contents

## Synthesis & Characteristics

All the starting chemicals are purchased from reagent manufacturers and are chemical pure without further purification unless specified.

### a) Characteristic Instruments and methods

- Nuclear Magnetic Resonance (NMR)

  $^1$H NMR was performed by Bruker Avance III 400MHz NMR Spectroscopy.

- Crystallography

  Crystallography data were obtained from Rigaku SuperNova, with CCD detector and X-ray source of Cu $K_\alpha$ (λ=1.54184Å). Crystal resolution were carried out by Olex2 program (ver.1.2.10) equipping ShelXL-2016 package.[1, 2]

- Thermodynamics Analysis

  Thermogravimetry - Differential Scanning Calorimeter (TG-DSC) diagram was performed by Mettler-Toledo TGA/DSC 1 STARe. The experiment was taken under nitrogen atmosphere. Alumina crucibles were used and the heating rate was 10°C / min.

- Photoluminescence properties

  Photoluminescent properties were measured by Horiba Jobin-Yvon FluoroMax-4 fluorescence spectrometer.
  The lifetime of each sample was characterized by Edinburgh Instruments FLS980 UV/V/NIR Fluorescence Spectrometer. 375 nm laser was served as the light source.

- Calculation

  The distribution of frontier molecule orbitals was obtained from Gaussian 09 program (version D.01)[3], and the charge density difference was calculated by Multiwfn 3.4.[4] All the diagrams were plotted by VMD.[5]

## b) Synthesis

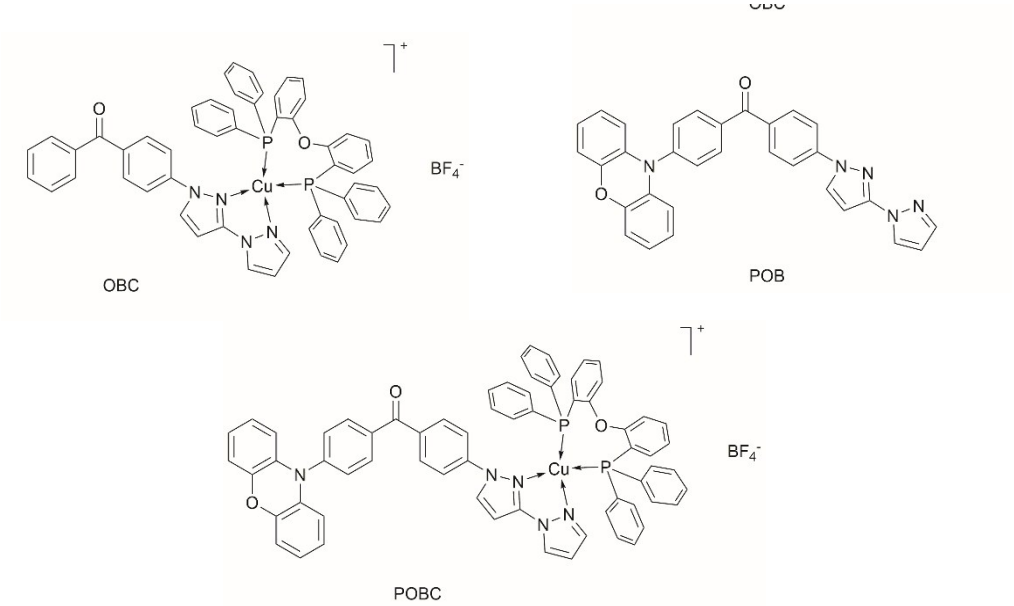



**Chart S1** Chemical structure of **OBC**, **POB**, and **POBC**.

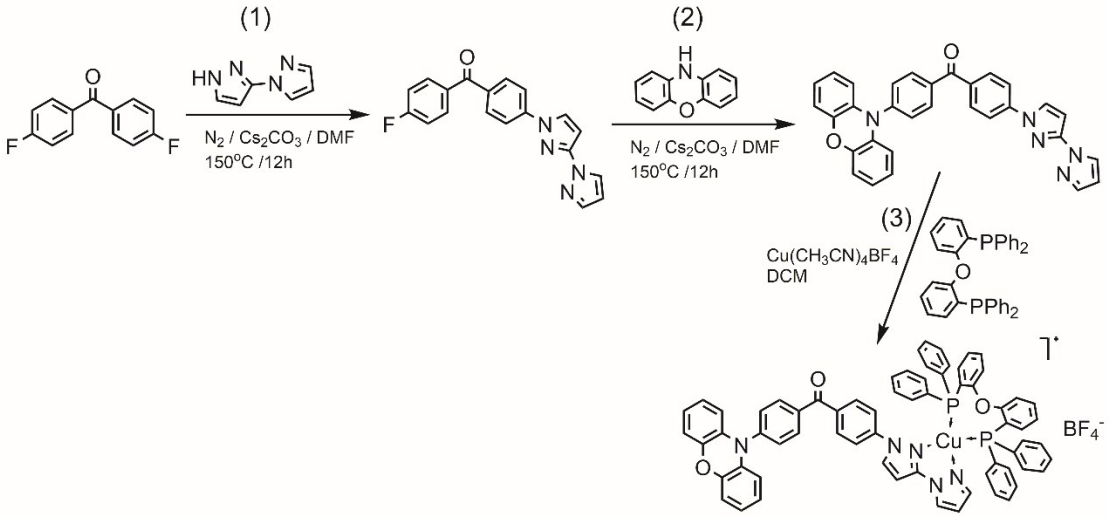
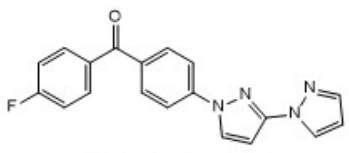



**Chart S2** Synthetic procedure of **POBC**.

- **(4-(1'H-[1,3'-bipyrazol]-1'-yl)phenyl)(4-fluorophenyl)methanone (FOB)**

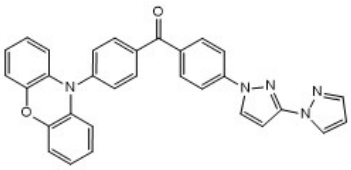



1'H-1,3'-bipyrazole (10 mmol) was obtained from previous report.[6] 4.89 g of $Cs_2CO_3$ (15 mmol), 1.34 g of 1'H-1,3'-bipyrazole (10 mmol) and 15mL of N,N-dimethylformamide (DMF) was added to a 100mL round Schlenk flask under the nitrogen atmosphere, and stirred for half an hour. 2.62 g of bis(4-fluorophenyl)methanone (12 mmol) was then added into the solution. The

mixture was heated to 150°C for 12 h. After cooled to room temperature, distilled water was poured into the mixture. After being filtered, the solid was washed by 25 mL of brine for 3 times and dissolved by 25 mL of dichloromethane, and dried with $MgSO_4$ and filtered. The filtered solvent was removed under reduced pressure. The powder was purified by silica column chromatography using hexane and ethyl acetate as eluent. The product yielded 2.90g (87.4%).

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.79 (s, 1H), 8.42 (s, 1H), 8.09 (s, 2H), 7.89 (d, *J* = 22.7 Hz, 4H), 7.80 (s, 1H), 7.43 (s, 2H), 6.90 (s, 1H), 6.58 (s, 1H). Elemental Analysis: N=16.57; C=69.03; H=3.65.

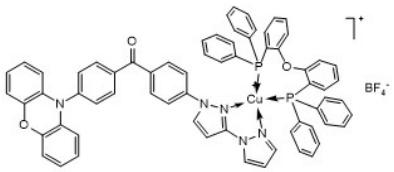
- **(4-(1'*H*-[1,3'-bipyrazol]-1'-yl) phenyl) (4-(10*H*-phenoxazin-10-yl)phenyl)methanone (POB)**


Chemical Formula: $C_{31}H_{21}N_5O_2$
Molecular Weight: 495.54

Similar to the reaction (1) in **Chart S2**. 10H-phenoxazine of 1.2 equivalent to **FOB** was added. The yellow product yielded 83.7%.

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.81 (s, 1H), 8.42 (s, 1H), 8.11 (s, 2H), 8.03 (s, 4H), 7.81 (s, 1H), 7.64 (s, 2H), 6.91 (s, 1H), 6.78 (s, 2H), 6.72 (s, 4H), 6.59 (s, 1H), 6.02 (s, 2H). Elemental Analysis: N=13.11; C=73.18; H=4.34

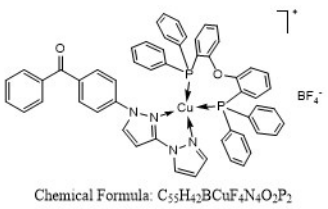
- **((4-(1'*H*-[1, 3'-bipyrazol]-1'-yl)phenyl) (4-(10H-phenoxazin-10-yl)phenyl)methanone)((oxybis(2,1-phenylene))bis(diphenylphosphane)) copper(I) tetrafluoro-borate (POBC)**


Chemical Formula: $C_{67}H_{49}BCuF_4N_5O_3P_2$
Molecular Weight: 1184.46

0.108 grams of (oxybis(2,1-phenylene))bis-(diphenylphosphane) (**POP**, 0.2 mmol) and 0.063 g of $Cu(CH_3CN)_4BF_4$ (0.2 mmol) were added into 10 mL of dichloromethane (DCM), and stirred for 10 minutes. Then 0.099 g of **POB** (0.2 mmol) was added to the solution and stirred for another 20 minutes. The final product was re-crystalized from the solution. The product yielded 0.139g (58.7%).

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.83 (d, *J* = 2.7 Hz, 1H), 8.48 (s, 1H), 8.06 (d, *J* = 8.3 Hz, 2H), 8.00 – 7.72 (m, 5H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.56 – 7.13 (m, 22H), 7.10 – 6.96 (m, 5H), 6.82 – 6.58 (m, 9H), 6.02 (dd, *J* = 7.5, 1.8 Hz, 2H). Elemental Analysis: N=5.84; C=67.90; H=4.16

- **((4-(1'*H*-[1, 3'-bipyrazol]-1'-yl)phenyl)(phenyl) methanone) ((oxybis(2,1-phenylene))bis(diphenylphosphane)) copper(I) tetrafluoroborate (OBC)**



Chemical Formula: $C_{55}H_{42}BCuF_4N_4O_2P_2$

Similar to the reaction (1) and (3) in **Chart S2**, except (4-fluorophenyl)(phenyl)methanone was used as the starting material instead of bis(4-fluorophenyl)methanone. The yield of re-crystalized **OBC** was 61.1%.

1H NMR (400 MHz, DMSO-d6) δ 8.81 (d, J = 2.8 Hz, 1H), 8.46 (s, 1H), 8.05 (d, J = 8.3 Hz, 2H), 7.89 – 7.68 (m, 6H), 7.60 (t, J = 7.6 Hz, 2H), 7.56 – 7.10 (m, 22H), 7.06 (t, J = 7.5 Hz, 2H), 6.99 (d, J = 8.2 Hz, 2H), 6.95 (s, 1H), 6.66 (d, J = 7.3 Hz, 2H), 6.61 (t, J = 2.2 Hz, 1H). Elemental Analysis: N=5.47; C=66.02; H=4.03

## Hydrogen Nuclear Magnetic Resonance ($^1$H NMR) Spectra

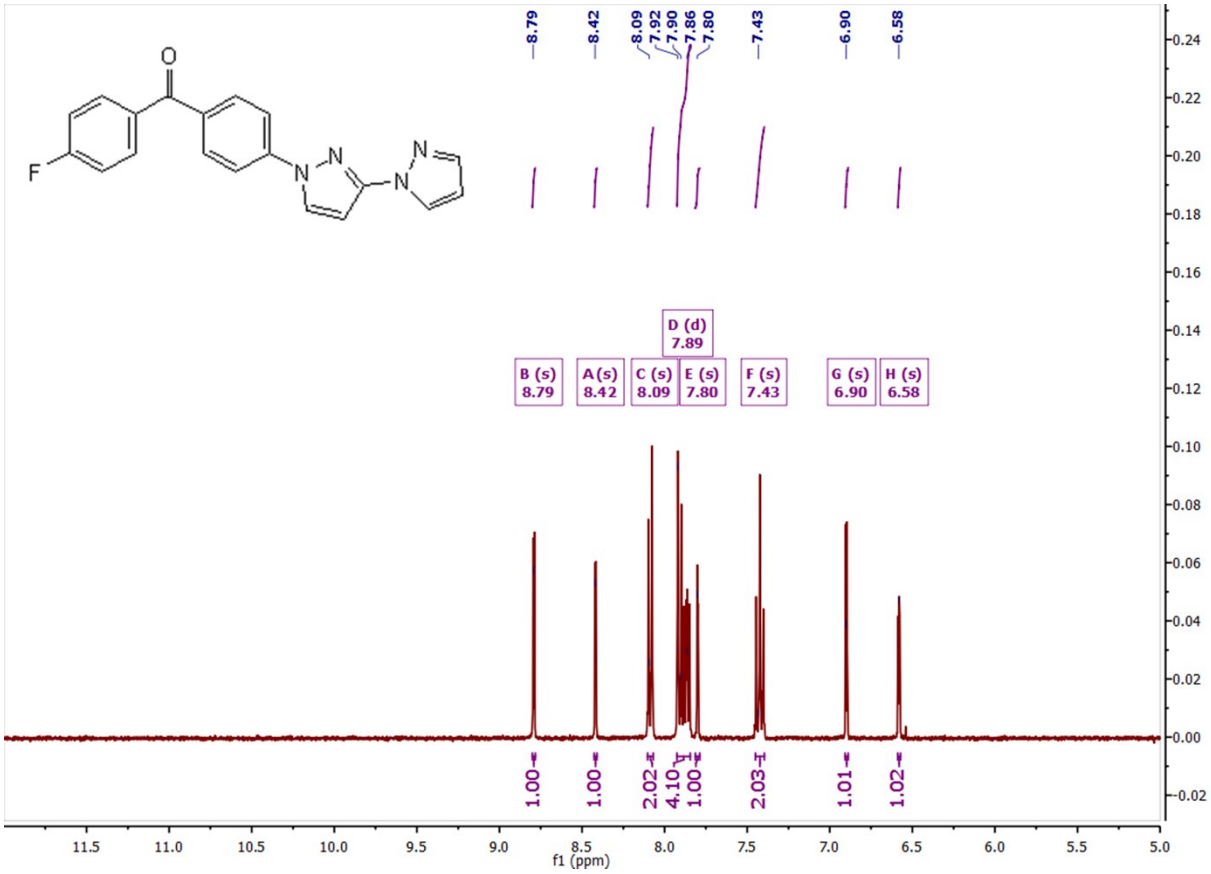



**Fig. S4** $^1$H NMR spectra of **FOB** (*d*$^6$-DMSO as solvent)

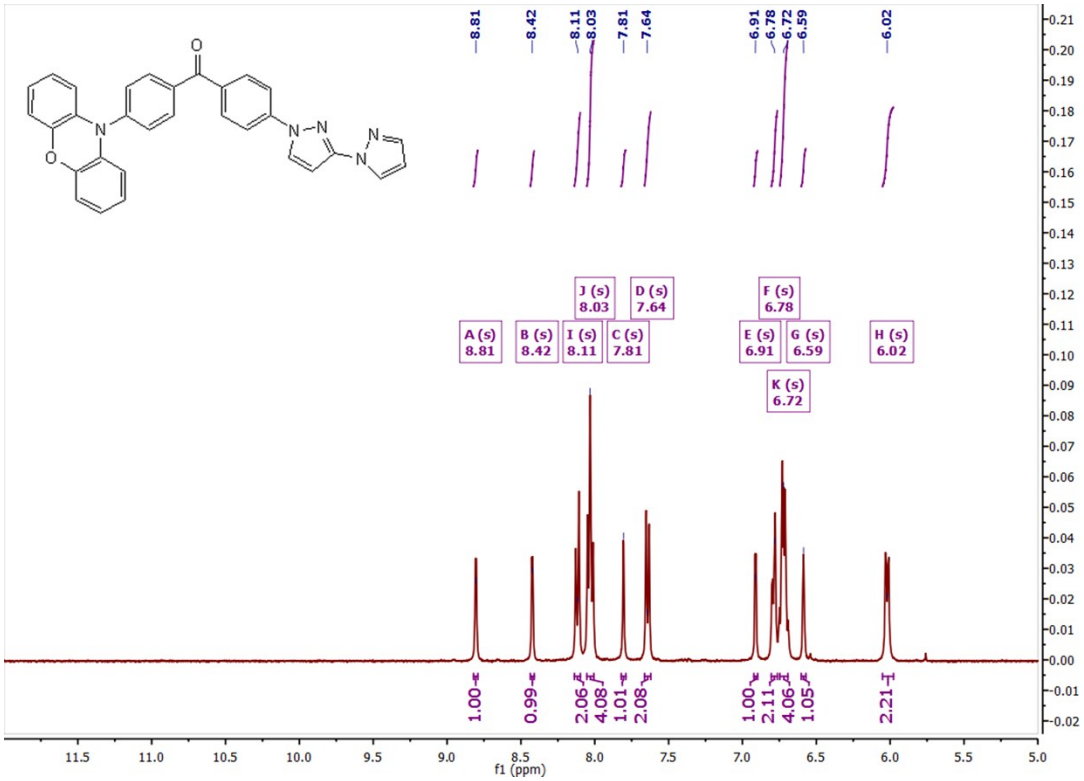



**Fig. S5** $^{1}$H NMR spectra of **POB** (*d*$^{6}$-DMSO as solvent)

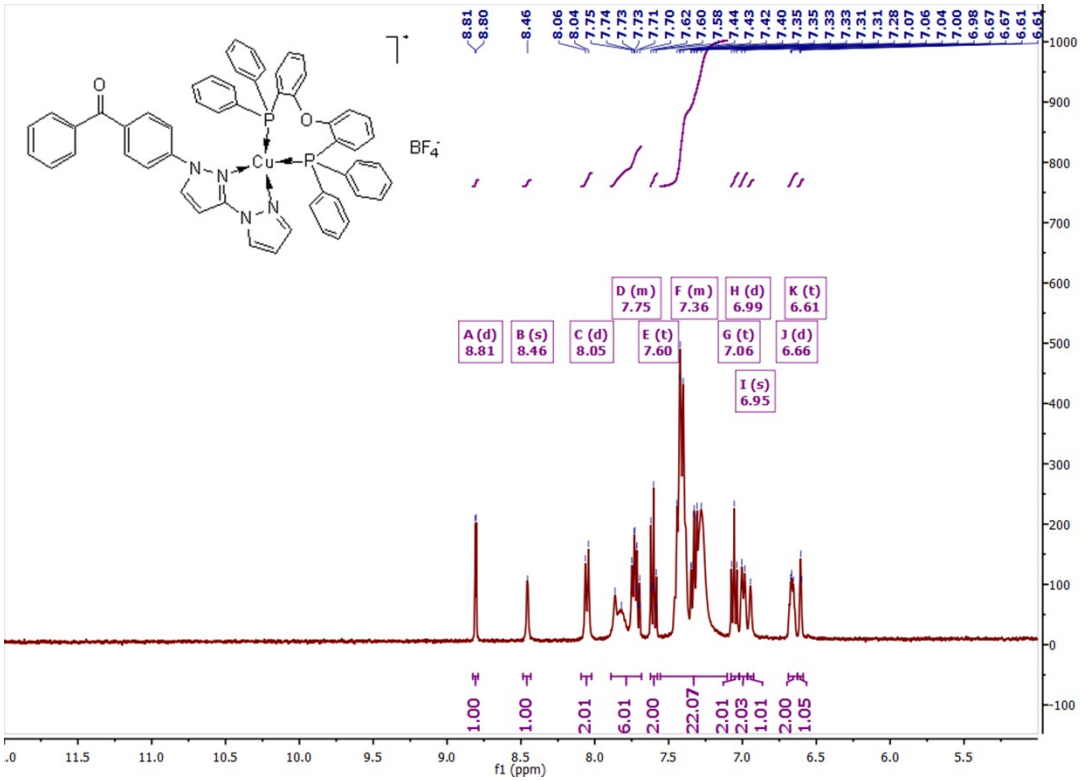



**Fig. S6** $^{1}$H NMR spectra of **OBC** (*d*$^{6}$-DMSO as solvent)

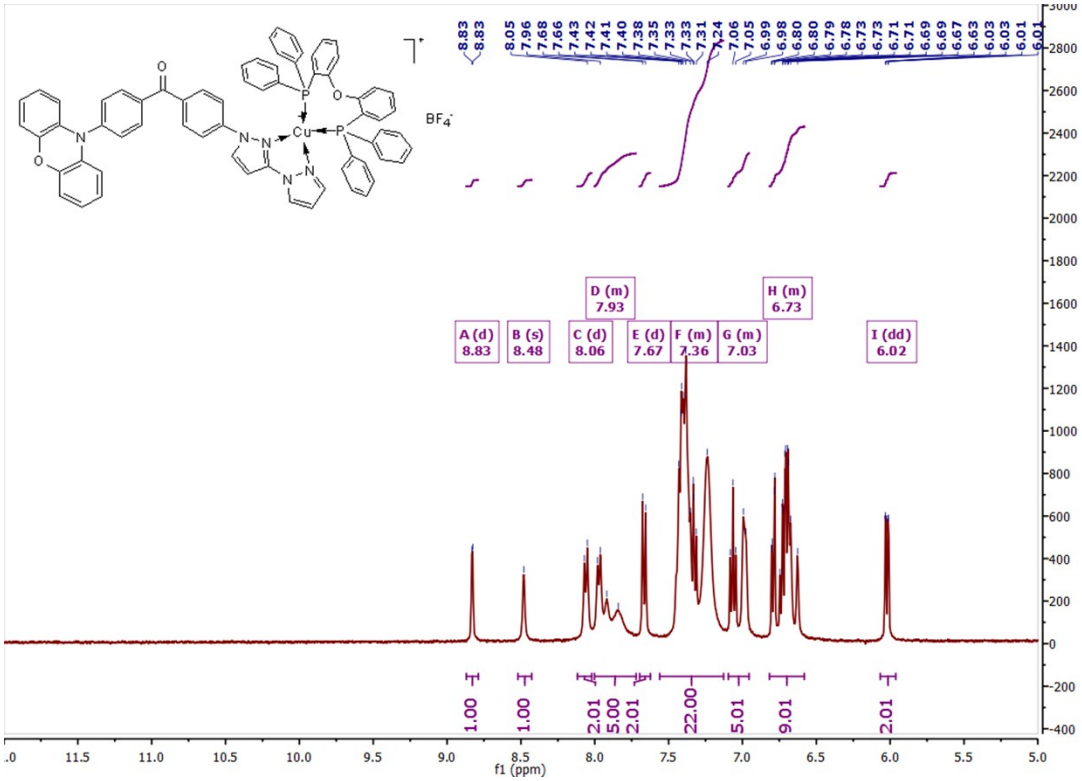



**Fig. S7** $^{1}$H NMR spectra of **POBC** (*d*$^{6}$-DMSO as solvent)

## X-ray Diffraction Crystallography

- **POB**

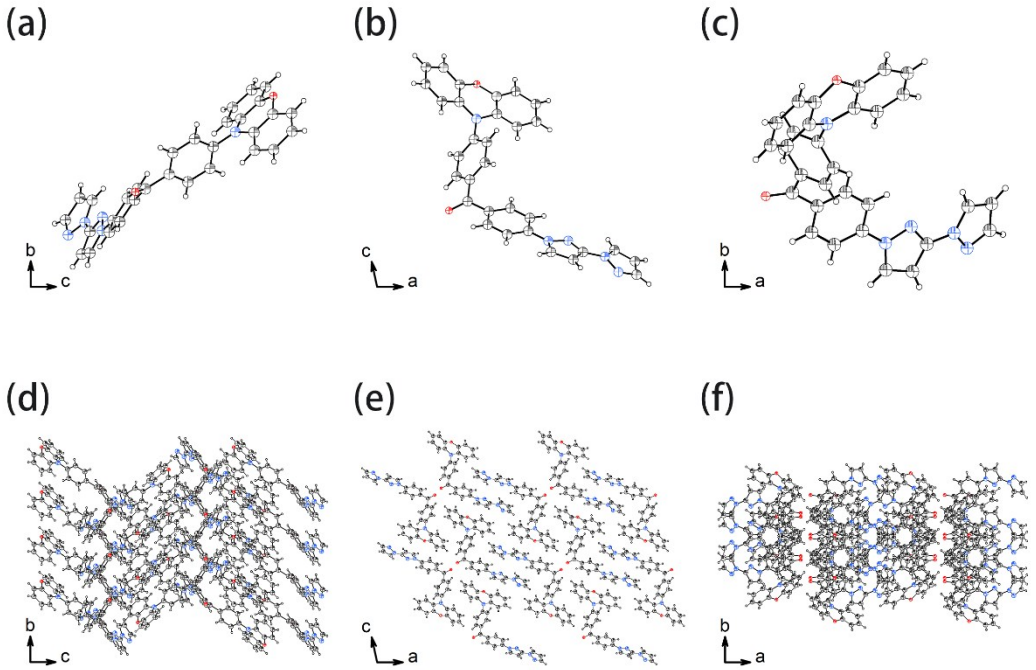



**Fig. S8 POB** viewing in different perspectives. (a)/(b)/(c) are the single molecule of POB viewing through a/b/c axis, while (d)/(e)/(f) are the stacked molecules viewing in the same direction to (a)/(b)/(c), respectively.

- **OBC**

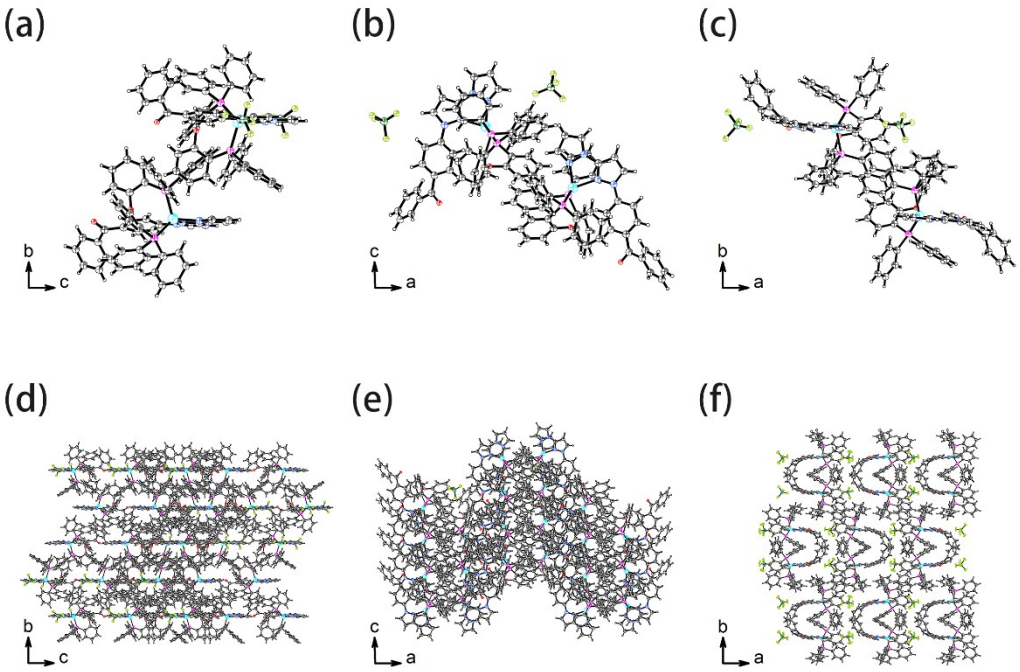



**Fig. S9** OBC viewing in different perspectives. (a)/(b)/(c) are the single molecule of OBC viewing through a/b/c axis, while (d)/(e)/(f) are the stacked molecules viewing in the same direction to (a)/(b)/(c), respectively.

- **POBC**

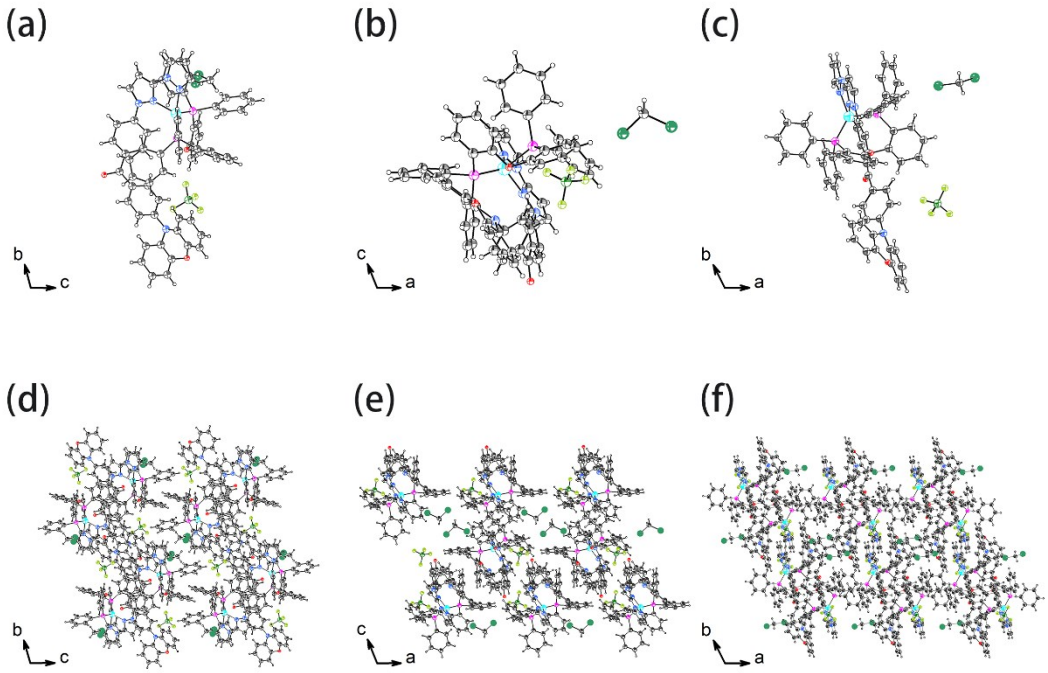



**Fig. S10** POBC viewing in different perspectives. (a)/(b)/(c) are the single molecule of POBC viewing through a/b/c axis, while (d)/(e)/(f) are the stacked molecules viewing in the same direction to (a)/(b)/(c), respectively. In Fig. S6(e), dichloromethane molecules are shown in the tunnels.

**Table 1 Crystal data and structure refinement for OBC**

| | |
|---|---|
| **Identification code** | 1864205_OBC |
| **Empirical formula** | $C_{55}H_{42}BCuF_4N_4O_2P_2$ |
| **Formula weight** | 1003.21 |
| **Temperature/K** | 100.0(2) |
| **Crystal system** | monoclinic |
| **Space group** | $P2_1/c$ |
| **a/Å** | 27.2797(2) |
| **b/Å** | 30.1904(3) |
| **c/Å** | 11.65080(10) |
| **α/°** | 90 |
| **β/°** | 91.3520(10) |
| **γ/°** | 90 |
| **Volume/Å³** | 9592.75(14) |
| **Z** | 8 |
| **$\rho_{calc}$g/cm³** | 1.389 |
| **μ/mm⁻¹** | 1.796 |
| **F(000)** | 4128.0 |
| **Crystal size/mm³** | 0.16 × 0.12 × 0.1 |
| **Radiation** | CuKα (λ = 1.54184) |
| **2Θ range for data collection/°** | 8.136 to 141.114 |
| **Index ranges** | -30 ≤ h ≤ 33, -36 ≤ k ≤ 32, -14 ≤ l ≤ 11 |
| **Reflections collected** | 60932 |
| **Independent reflections** | 18213 [$R_{int}$ = 0.0380, $R_{sigma}$ = 0.0318] |
| **Data/restraints/parameters** | 18213/24/1300 |
| **Goodness-of-fit on F²** | 1.171 |
| **Final R indexes [I>=2σ (I)]** | $R_1$ = 0.0612, $wR_2$ = 0.1488 |
| **Final R indexes [all data]** | $R_1$ = 0.0672, $wR_2$ = 0.1518 |
| **Largest diff. peak/hole / e Å⁻³** | 1.42/-0.45 |

**Table 2 Selected Bond Lengths for OBC**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Cu10 | P101 | 2.2819(10) | P202 | C243 | 1.822(4) |
| Cu10 | P102 | 2.2337(10) | P202 | C244 | 1.826(4) |
| Cu10 | N101 | 2.073(3) | P202 | C250 | 1.825(4) |
| Cu10 | N103 | 2.157(3) | O201 | C213 | 1.226(5) |
| P101 | C120 | 1.820(4) | O202 | C237 | 1.401(4) |
| P101 | C126 | 1.819(4) | O202 | C238 | 1.397(4) |
| P101 | C132 | 1.833(4) | N201 | N202 | 1.363(4) |
| P102 | C143 | 1.827(3) | N201 | C201 | 1.328(5) |
| P102 | C144 | 1.822(4) | N202 | C203 | 1.353(4) |
| P102 | C150 | 1.825(4) | N202 | C204 | 1.397(4) |
| O101 | C113 | 1.228(6) | N203 | N204 | 1.372(4) |
| O102 | C137 | 1.400(4) | N203 | C204 | 1.322(4) |
| O102 | C138 | 1.405(4) | N204 | C206 | 1.355(4) |
| N101 | N102 | 1.363(4) | N204 | C207 | 1.415(4) |
| N101 | C101 | 1.330(5) | C201 | C202 | 1.400(5) |
| N102 | C103 | 1.360(5) | C202 | C203 | 1.377(6) |
| N102 | C104 | 1.391(4) | C204 | C205 | 1.400(5) |
| N103 | N104 | 1.370(4) | C205 | C206 | 1.358(5) |
| N103 | C104 | 1.321(4) | C207 | C208 | 1.399(5) |
| N104 | C106 | 1.357(4) | C207 | C212 | 1.394(5) |
| N104 | C107 | 1.413(4) | C208 | C209 | 1.381(5) |
| C101 | C102 | 1.406(6) | C209 | C210 | 1.394(5) |
| C102 | C103 | 1.362(6) | C210 | C211 | 1.390(5) |
| C104 | C105 | 1.391(5) | C210 | C213 | 1.482(5) |
| C105 | C106 | 1.371(5) | C211 | C212 | 1.377(5) |
| C107 | C108 | 1.398(5) | C213 | C214 | 1.491(5) |
| C107 | C112 | 1.394(5) | C214 | C215 | 1.391(6) |
| C108 | C109 | 1.376(5) | C214 | C219 | 1.393(5) |
| C109 | C110 | 1.390(5) | C215 | C216 | 1.393(6) |
| C110 | C111 | 1.395(5) | C216 | C217 | 1.389(7) |
| C110 | C113 | 1.476(5) | C217 | C218 | 1.386(8) |
| C111 | C112 | 1.374(5) | C218 | C219 | 1.389(6) |
| C113 | C114 | 1.500(6) | C220 | C221 | 1.374(5) |
| C114 | C115 | 1.404(8) | C220 | C225 | 1.388(6) |
| C114 | C119 | 1.394(7) | C221 | C222 | 1.397(6) |
| C115 | C116 | 1.390(7) | C222 | C223 | 1.371(6) |
| C116 | C117 | 1.380(10) | C223 | C224 | 1.366(7) |

**Table 3 Selected Bond Angles for OBC**

| Atom | Atom | Atom | Angle/˚ | Atom | Atom | Atom | Angle/˚ |
|---|---|---|---|---|---|---|---|
| P102 | Cu10 | P101 | 113.32(4) | C243 | P202 | Cu20 | 109.23(12) |
| N101 | Cu10 | P101 | 106.91(9) | C243 | P202 | C244 | 103.10(16) |
| N101 | Cu10 | P102 | 122.88(9) | C243 | P202 | C250 | 104.85(16) |
| N101 | Cu10 | N103 | 78.24(11) | C244 | P202 | Cu20 | 117.39(13) |
| N103 | Cu10 | P101 | 110.82(8) | C250 | P202 | Cu20 | 117.10(12) |
| N103 | Cu10 | P102 | 119.78(8) | C250 | P202 | C244 | 103.63(17) |
| C120 | P101 | Cu10 | 107.76(12) | C238 | O202 | C237 | 118.6(3) |
| C120 | P101 | C132 | 103.46(17) | N202 | N201 | Cu20 | 113.0(2) |
| C126 | P101 | Cu10 | 115.01(13) | C201 | N201 | Cu20 | 142.3(3) |
| C126 | P101 | C120 | 103.58(17) | C201 | N201 | N202 | 104.4(3) |
| C126 | P101 | C132 | 103.80(17) | N201 | N202 | C204 | 118.3(3) |
| C132 | P101 | Cu10 | 121.34(12) | C203 | N202 | N201 | 112.4(3) |
| C143 | P102 | Cu10 | 108.56(11) | C203 | N202 | C204 | 129.3(3) |
| C144 | P102 | Cu10 | 118.22(13) | N204 | N203 | Cu20 | 144.4(2) |
| C144 | P102 | C143 | 102.20(16) | C204 | N203 | Cu20 | 111.7(2) |
| C144 | P102 | C150 | 104.01(17) | C204 | N203 | N204 | 103.9(3) |
| C150 | P102 | Cu10 | 117.70(11) | N203 | N204 | C207 | 121.1(3) |
| C150 | P102 | C143 | 104.27(16) | C206 | N204 | N203 | 110.7(3) |
| C137 | O102 | C138 | 116.2(3) | C206 | N204 | C207 | 128.2(3) |
| N102 | N101 | Cu10 | 113.0(2) | N201 | C201 | C202 | 111.7(3) |
| C101 | N101 | Cu10 | 142.6(3) | C203 | C202 | C201 | 105.3(3) |
| C101 | N101 | N102 | 104.4(3) | N202 | C203 | C202 | 106.2(3) |
| N101 | N102 | C104 | 118.6(3) | N202 | C204 | C205 | 128.5(3) |
| C103 | N102 | N101 | 112.2(3) | N203 | C204 | N202 | 118.4(3) |
| C103 | N102 | C104 | 129.1(3) | N203 | C204 | C205 | 113.1(3) |
| N104 | N103 | Cu10 | 144.2(2) | C206 | C205 | C204 | 103.7(3) |
| C104 | N103 | Cu10 | 111.9(2) | N204 | C206 | C205 | 108.5(3) |
| C104 | N103 | N104 | 103.9(3) | C208 | C207 | N204 | 119.1(3) |
| N103 | N104 | C107 | 121.6(3) | C212 | C207 | N204 | 121.0(3) |
| C106 | N104 | N103 | 110.8(3) | C212 | C207 | C208 | 119.9(3) |
| C106 | N104 | C107 | 127.5(3) | C209 | C208 | C207 | 119.2(3) |
| N101 | C101 | C102 | 111.2(4) | C208 | C209 | C210 | 121.2(3) |
| C103 | C102 | C101 | 105.9(3) | C209 | C210 | C213 | 123.6(3) |
| N102 | C103 | C102 | 106.2(4) | C211 | C210 | C209 | 118.6(3) |
| N102 | C104 | C105 | 128.0(3) | C211 | C210 | C213 | 117.8(3) |
| N103 | C104 | N102 | 118.3(3) | C212 | C211 | C210 | 121.0(3) |
| N103 | C104 | C105 | 113.7(3) | C211 | C212 | C207 | 119.8(3) |

**Table 4 Crystal data and structure refinement for POB**

| | |
|---|---|
| **Identification code** | 1864206_POB |
| **Empirical formula** | $C_{31}H_{21}N_5O_2$ |
| **Formula weight** | 495.53 |
| **Temperature/K** | 100.0(2) |
| **Crystal system** | monoclinic |
| **Space group** | $P2_1/c$ |
| **a/Å** | 17.7416(4) |
| **b/Å** | 5.58580(10) |
| **c/Å** | 24.5679(8) |
| **α/°** | 90 |
| **β/°** | 102.175(3) |
| **γ/°** | 90 |
| **Volume/Å³** | 2379.94(11) |
| **Z** | 4 |
| **$\rho_{calc}$g/cm³** | 1.383 |
| **μ/mm⁻¹** | 0.718 |
| **F(000)** | 1032.0 |
| **Crystal size/mm³** | 0.28 × 0.26 × 0.15 |
| **Radiation** | CuKα (λ = 1.54184) |
| **2Θ range for data collection/°** | 7.362 to 148.982 |
| **Index ranges** | -21 ≤ h ≤ 17, -6 ≤ k ≤ 6, -28 ≤ l ≤ 30 |
| **Reflections collected** | 8865 |
| **Independent reflections** | 4701 [$R_{int}$ = 0.0233, $R_{sigma}$ = 0.0334] |
| **Data/restraints/parameters** | 4701/0/343 |
| **Goodness-of-fit on F²** | 1.058 |
| **Final R indexes [I>=2σ (I)]** | $R_1$ = 0.0369, $wR_2$ = 0.0883 |
| **Final R indexes [all data]** | $R_1$ = 0.0452, $wR_2$ = 0.0943 |
| **Largest diff. peak/hole / e Å⁻³** | 0.20/-0.27 |

**Table 5 Bond Lengths for POB**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| O001 | C00H | 1.2204(16) | C00B | C00P | 1.3878(18) |
| O002 | C00Q | 1.3851(18) | C00C | C00F | 1.3827(18) |
| O002 | C00U | 1.3887(18) | C00D | C00M | 1.3948(18) |
| N003 | N004 | 1.3679(15) | C00D | C00P | 1.3888(19) |
| N003 | C008 | 1.4144(16) | C00E | C00S | 1.3864(18) |
| N003 | C00I | 1.3618(17) | C00G | C00I | 1.3697(19) |
| N004 | C00N | 1.3241(17) | C00G | C00N | 1.4035(19) |
| N005 | N007 | 1.3625(15) | C00J | C00O | 1.3671(19) |
| N005 | C00J | 1.3604(18) | C00K | C00M | 1.3918(18) |
| N005 | C00N | 1.4011(16) | C00L | C00T | 1.3926(19) |
| N006 | C00D | 1.4270(16) | C00L | C00U | 1.4003(19) |
| N006 | C00L | 1.4086(17) | C00O | C00R | 1.404(2) |
| N006 | C00V | 1.4083(16) | C00Q | C00V | 1.4000(19) |
| N007 | C00R | 1.3280(18) | C00Q | C00X | 1.3770(19) |
| C008 | C00C | 1.3942(18) | C00T | C00Y | 1.393(2) |
| C008 | C00S | 1.3975(18) | C00U | C011 | 1.377(2) |
| C009 | C00B | 1.3959(17) | C00V | C00Z | 1.389(2) |
| C009 | C00H | 1.4990(17) | C00W | C00X | 1.394(2) |
| C009 | C00K | 1.3983(19) | C00W | C010 | 1.381(2) |
| C00A | C00E | 1.3968(19) | C00Y | C012 | 1.385(2) |
| C00A | C00F | 1.3999(18) | C00Z | C010 | 1.396(2) |
| C00A | C00H | 1.4923(17) | C011 | C012 | 1.393(2) |

**Table 6 Bond Angles for POB**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C00Q | O002 | C00U | 116.30(11) | N003 | C00I | C00G | 107.67(12) |
| N004 | N003 | C008 | 119.37(10) | N005 | C00J | C00O | 106.61(12) |
| C00I | N003 | N004 | 111.66(10) | C00M | C00K | C009 | 119.78(12) |
| C00I | N003 | C008 | 128.91(11) | C00T | C00L | N006 | 124.03(12) |
| C00N | N004 | N003 | 103.48(10) | C00T | C00L | C00U | 117.80(12) |
| N007 | N005 | C00N | 118.99(11) | C00U | C00L | N006 | 118.08(12) |
| C00J | N005 | N007 | 112.40(11) | C00K | C00M | C00D | 120.20(12) |
| C00J | N005 | C00N | 128.00(11) | N004 | C00N | N005 | 119.28(12) |
| C00L | N006 | C00D | 121.24(11) | N004 | C00N | C00G | 113.60(11) |
| C00V | N006 | C00D | 120.53(11) | N005 | C00N | C00G | 126.98(12) |
| C00V | N006 | C00L | 117.83(11) | C00J | C00O | C00R | 104.83(12) |
| C00R | N007 | N005 | 103.71(11) | C00B | C00P | C00D | 119.73(12) |
| C00C | C008 | N003 | 119.38(11) | O002 | C00Q | C00V | 121.02(12) |
| C00C | C008 | C00S | 120.49(12) | C00X | C00Q | O002 | 117.34(13) |
| C00S | C008 | N003 | 120.13(11) | C00X | C00Q | C00V | 121.63(14) |
| C00B | C009 | C00H | 120.62(11) | N007 | C00R | C00O | 112.44(12) |
| C00B | C009 | C00K | 119.50(12) | C00E | C00S | C008 | 119.67(12) |
| C00K | C009 | C00H | 119.88(11) | C00L | C00T | C00Y | 120.94(14) |
| C00E | C00A | C00F | 118.97(12) | O002 | C00U | C00L | 121.61(12) |
| C00E | C00A | C00H | 119.72(11) | C011 | C00U | O002 | 116.67(13) |
| C00F | C00A | C00H | 121.28(12) | C011 | C00U | C00L | 121.56(14) |
| C00P | C00B | C009 | 120.64(12) | C00Q | C00V | N006 | 118.76(12) |
| C00F | C00C | C008 | 119.25(11) | C00Z | C00V | N006 | 123.03(12) |
| C00M | C00D | N006 | 119.25(12) | C00Z | C00V | C00Q | 118.21(13) |
| C00P | C00D | N006 | 120.64(12) | C010 | C00W | C00X | 119.69(13) |
| C00P | C00D | C00M | 120.12(12) | C00Q | C00X | C00W | 119.58(14) |
| C00S | C00E | C00A | 120.51(11) | C012 | C00Y | C00T | 120.25(15) |
| C00C | C00F | C00A | 121.11(12) | C00V | C00Z | C010 | 120.43(14) |
| C00I | C00G | C00N | 103.59(12) | C00W | C010 | C00Z | 120.44(15) |
| O001 | C00H | C009 | 120.88(11) | C00U | C011 | C012 | 120.01(14) |
| O001 | C00H | C00A | 121.39(12) | C00Y | C012 | C011 | 119.43(14) |
| C00A | C00H | C009 | 117.73(10) | | | | |

**Table 7 Crystal data and structure refinement for POBC (grown in EtOH)**

| | |
|---|---|
| **Identification code** | 1864207_POBC_EtOH |
| **Empirical formula** | $C_{67}H_{49}CuN_5O_3P_2BF_4$ |
| **Formula weight** | 1184.40 |
| **Temperature/K** | 100.00(16) |
| **Crystal system** | triclinic |
| **Space group** | P-1 |
| **a/Å** | 14.8651(7) |
| **b/Å** | 15.2844(6) |
| **c/Å** | 16.9100(5) |
| **α/°** | 96.249(3) |
| **β/°** | 107.674(3) |
| **γ/°** | 114.228(4) |
| **Volume/Å$^3$** | 3215.5(2) |
| **Z** | 2 |
| **$\rho_{calc}$g/cm$^3$** | 1.223 |
| **μ/mm$^{-1}$** | 1.437 |
| **F(000)** | 1220.0 |
| **Crystal size/mm$^3$** | 0.29 × 0.15 × 0.09 |
| **Radiation** | CuKα (λ = 1.54184) |
| **2Θ range for data collection/°** | 6.584 to 149.376 |
| **Index ranges** | -18 ≤ h ≤ 16, -17 ≤ k ≤ 19, -18 ≤ l ≤ 21 |
| **Reflections collected** | 23544 |
| **Independent reflections** | 12789 [$R_{int}$ = 0.0288, $R_{sigma}$ = 0.0371] |
| **Data/restraints/parameters** | 12789/0/748 |
| **Goodness-of-fit on F$^2$** | 1.037 |
| **Final R indexes [I>=2σ (I)]** | $R_1$ = 0.0353, w$R_2$ = 0.0885 |
| **Final R indexes [all data]** | $R_1$ = 0.0429, w$R_2$ = 0.0933 |
| **Largest diff. peak/hole / e Å$^{-3}$** | 0.33/-0.50 |

**Table 8 Selected Bond Lengths for POBC (grown in EtOH)**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Cu1 | P1 | 2.3015(5) | C21 | C22 | 1.397(3) |
| Cu1 | P2 | 2.2138(5) | C22 | C23 | 1.380(3) |
| Cu1 | N3 | 2.1092(13) | C23 | C24 | 1.394(3) |
| Cu1 | N5 | 2.0689(14) | C24 | C25 | 1.395(3) |
| P1 | C32 | 1.8218(17) | C26 | C27 | 1.369(2) |
| P1 | C38 | 1.8265(16) | C27 | C28 | 1.399(2) |
| P1 | C44 | 1.8358(16) | C29 | C30 | 1.370(3) |
| P2 | C55 | 1.8238(16) | C30 | C31 | 1.397(2) |
| P2 | C56 | 1.8215(16) | C32 | C33 | 1.398(2) |
| P2 | C62 | 1.8208(17) | C32 | C37 | 1.398(2) |
| O1 | C1 | 1.220(2) | C33 | C34 | 1.390(2) |
| O2 | C49 | 1.403(2) | C34 | C35 | 1.386(3) |
| O2 | C50 | 1.3922(19) | C35 | C36 | 1.383(3) |
| O3 | C19 | 1.391(3) | C36 | C37 | 1.390(2) |
| O3 | C20 | 1.388(2) | C38 | C39 | 1.389(2) |
| N1 | C5 | 1.445(2) | C38 | C43 | 1.392(2) |
| N1 | C14 | 1.419(2) | C39 | C40 | 1.391(2) |
| N1 | C25 | 1.406(3) | C40 | C41 | 1.380(3) |
| N2 | N3 | 1.3662(18) | C41 | C42 | 1.381(3) |
| N2 | C11 | 1.419(2) | C42 | C43 | 1.396(2) |
| N2 | C26 | 1.362(2) | C44 | C45 | 1.400(2) |
| N3 | C28 | 1.328(2) | C44 | C49 | 1.396(2) |
| N4 | N5 | 1.3688(19) | C45 | C46 | 1.390(2) |
| N4 | C28 | 1.401(2) | C46 | C47 | 1.386(3) |
| N4 | C29 | 1.355(2) | C47 | C48 | 1.392(3) |
| N5 | C31 | 1.329(2) | C48 | C49 | 1.387(2) |
| C1 | C2 | 1.496(2) | C50 | C51 | 1.386(2) |
| C1 | C8 | 1.493(2) | C50 | C55 | 1.401(2) |
| C2 | C3 | 1.396(2) | C51 | C52 | 1.394(2) |
| C2 | C7 | 1.393(3) | C52 | C53 | 1.382(3) |
| C3 | C4 | 1.386(2) | C53 | C54 | 1.394(2) |
| C4 | C5 | 1.389(3) | C54 | C55 | 1.398(2) |
| C5 | C6 | 1.383(2) | C56 | C57 | 1.391(2) |
| C6 | C7 | 1.398(3) | C56 | C61 | 1.401(2) |
| C8 | C9 | 1.404(2) | C57 | C58 | 1.385(2) |
| C8 | C13 | 1.396(2) | C58 | C59 | 1.390(2) |
| C9 | C10 | 1.386(2) | C59 | C60 | 1.382(3) |

**Table 9 Selected Bond Angles for POBC (grown in EtOH)**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| P2 | Cu1 | P1 | 117.750(17) | C23 | C22 | C21 | 119.3(2) |
| N3 | Cu1 | P1 | 101.29(4) | C22 | C23 | C24 | 120.5(2) |
| N3 | Cu1 | P2 | 125.91(4) | C23 | C24 | C25 | 120.64(19) |
| N5 | Cu1 | P1 | 100.02(4) | C20 | C25 | N1 | 118.58(17) |
| N5 | Cu1 | P2 | 125.06(4) | C24 | C25 | N1 | 123.33(17) |
| N5 | Cu1 | N3 | 78.26(5) | C24 | C25 | C20 | 118.08(19) |
| C32 | P1 | Cu1 | 105.26(5) | N2 | C26 | C27 | 108.00(15) |
| C32 | P1 | C38 | 105.29(8) | C26 | C27 | C28 | 103.68(14) |
| C32 | P1 | C44 | 103.53(8) | N3 | C28 | N4 | 116.61(14) |
| C38 | P1 | Cu1 | 115.44(6) | N3 | C28 | C27 | 113.26(15) |
| C38 | P1 | C44 | 102.73(7) | C27 | C28 | N4 | 130.12(15) |
| C44 | P1 | Cu1 | 122.84(5) | N4 | C29 | C30 | 106.73(15) |
| C55 | P2 | Cu1 | 107.50(5) | C29 | C30 | C31 | 105.51(16) |
| C56 | P2 | Cu1 | 119.14(6) | N5 | C31 | C30 | 111.53(16) |
| C56 | P2 | C55 | 105.88(7) | C33 | C32 | P1 | 119.73(13) |
| C62 | P2 | Cu1 | 118.07(6) | C37 | C32 | P1 | 120.44(12) |
| C62 | P2 | C55 | 103.51(8) | C37 | C32 | C33 | 118.69(16) |
| C62 | P2 | C56 | 101.16(8) | C34 | C33 | C32 | 120.60(16) |
| C50 | O2 | C49 | 116.09(12) | C35 | C34 | C33 | 120.10(17) |
| C20 | O3 | C19 | 115.14(15) | C36 | C35 | C34 | 119.83(17) |
| C14 | N1 | C5 | 117.90(16) | C35 | C36 | C37 | 120.43(17) |
| C25 | N1 | C5 | 116.93(15) | C36 | C37 | C32 | 120.35(16) |
| C25 | N1 | C14 | 116.56(16) | C39 | C38 | P1 | 122.43(13) |
| N3 | N2 | C11 | 120.28(13) | C39 | C38 | C43 | 119.07(15) |
| C26 | N2 | N3 | 111.13(13) | C43 | C38 | P1 | 118.43(13) |
| C26 | N2 | C11 | 128.57(14) | C38 | C39 | C40 | 119.74(18) |
| N2 | N3 | Cu1 | 141.71(10) | C41 | C40 | C39 | 120.87(19) |
| C28 | N3 | Cu1 | 113.67(11) | C40 | C41 | C42 | 119.98(16) |
| C28 | N3 | N2 | 103.93(13) | C41 | C42 | C43 | 119.40(18) |
| N5 | N4 | C28 | 117.90(13) | C38 | C43 | C42 | 120.93(18) |
| C29 | N4 | N5 | 111.63(14) | C45 | C44 | P1 | 121.72(12) |
| C29 | N4 | C28 | 130.45(15) | C49 | C44 | P1 | 120.85(12) |
| N4 | N5 | Cu1 | 112.87(10) | C49 | C44 | C45 | 117.42(15) |
| C31 | N5 | Cu1 | 142.04(12) | C46 | C45 | C44 | 121.11(16) |
| C31 | N5 | N4 | 104.60(13) | C47 | C46 | C45 | 120.16(16) |

**Table 10 Crystal data and structure refinement for POBC (grown in DCM/Ether)**

| | |
|---|---|
| **Identification code** | 1864278_POBC_DCM |
| **Empirical formula** | $C_{67}H_{49}CuN_5O_3P_2BF_4 \cdot CH_2Cl_2$ |
| **Formula weight** | 1269.32 |
| **Temperature/K** | 99.99(17) |
| **Crystal system** | triclinic |
| **Space group** | P-1 |
| **a/Å** | 14.5410(5) |
| **b/Å** | 15.2405(4) |
| **c/Å** | 16.9377(6) |
| **α/°** | 96.877(3) |
| **β/°** | 106.932(3) |
| **γ/°** | 113.006(3) |
| **Volume/Å³** | 3186.9(2) |
| **Z** | 2 |
| **$\rho_{calc}$g/cm³** | 1.323 |
| **μ/mm⁻¹** | 2.238 |
| **F(000)** | 1304.0 |
| **Crystal size/mm³** | 0.23 × 0.21 × 0.14 |
| **Radiation** | CuKα (λ = 1.54184) |
| **2Θ range for data collection/°** | 7.108 to 149.58 |
| **Index ranges** | -18 ≤ h ≤ 17, -8 ≤ k ≤ 18, -21 ≤ l ≤ 19 |
| **Reflections collected** | 22764 |
| **Independent reflections** | 12639 [$R_{int}$ = 0.0274, $R_{sigma}$ = 0.0381] |
| **Data/restraints/parameters** | 12639/69/763 |
| **Goodness-of-fit on F²** | 1.022 |
| **Final R indexes [I>=2σ (I)]** | $R_1$ = 0.0432, $wR_2$ = 0.1197 |
| **Final R indexes [all data]** | $R_1$ = 0.0508, $wR_2$ = 0.1265 |
| **Largest diff. peak/hole / e Å⁻³** | 0.52/-1.29 |

**Table 11 Selected Bond Lengths for POBC (grown in DCM/Ether)**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Cu1 | P8 | 2.3004(6) | C22 | C23 | 1.383(4) |
| Cu1 | P28 | 2.2127(6) | C23 | C24 | 1.390(4) |
| Cu1 | N2 | 2.0657(18) | C24 | C25 | 1.393(4) |
| Cu1 | N4 | 2.1065(17) | C26 | C27 | 1.371(3) |
| P8 | C32 | 1.824(2) | C27 | C28 | 1.401(3) |
| P8 | C38 | 1.829(2) | C29 | C30 | 1.369(3) |
| P8 | C44 | 1.835(2) | C30 | C31 | 1.401(3) |
| P28 | C55 | 1.824(2) | C32 | C33 | 1.398(3) |
| P28 | C56 | 1.823(2) | C32 | C37 | 1.398(3) |
| P28 | C62 | 1.821(2) | C33 | C34 | 1.394(3) |
| O1 | C1 | 1.222(3) | C34 | C35 | 1.382(4) |
| O2 | C19 | 1.377(3) | C35 | C36 | 1.387(4) |
| O2 | C20 | 1.397(4) | C36 | C37 | 1.388(3) |
| O3 | C49 | 1.398(3) | C38 | C39 | 1.399(3) |
| O3 | C50 | 1.393(3) | C38 | C43 | 1.395(3) |
| N1 | C11 | 1.437(3) | C39 | C40 | 1.392(3) |
| N1 | C14 | 1.439(2) | C40 | C41 | 1.387(4) |
| N1 | C25 | 1.402(4) | C41 | C42 | 1.381(4) |
| N2 | N3 | 1.366(2) | C42 | C43 | 1.397(3) |
| N2 | C31 | 1.329(3) | C44 | C45 | 1.401(3) |
| N3 | C28 | 1.403(3) | C44 | C49 | 1.400(3) |
| N3 | C29 | 1.354(3) | C45 | C46 | 1.389(3) |
| N4 | N5 | 1.364(2) | C46 | C47 | 1.384(4) |
| N4 | C28 | 1.327(3) | C47 | C48 | 1.391(3) |
| N5 | C5 | 1.419(3) | C48 | C49 | 1.391(3) |
| N5 | C26 | 1.360(3) | C50 | C51 | 1.390(3) |
| C1 | C2 | 1.496(3) | C50 | C55 | 1.394(3) |
| C1 | C8 | 1.497(3) | C51 | C52 | 1.390(3) |
| C2 | C3 | 1.401(3) | C52 | C53 | 1.376(3) |
| C2 | C7 | 1.397(3) | C53 | C54 | 1.393(3) |
| C3 | C4 | 1.387(3) | C54 | C55 | 1.398(3) |
| C4 | C5 | 1.395(3) | C56 | C57 | 1.402(3) |
| C5 | C6 | 1.388(3) | C56 | C61 | 1.393(3) |
| C6 | C7 | 1.387(3) | C57 | C58 | 1.385(3) |
| C8 | C9 | 1.395(3) | C58 | C59 | 1.390(4) |
| C8 | C13 | 1.398(3) | C59 | C60 | 1.387(3) |
| C9 | C10 | 1.387(3) | C60 | C61 | 1.400(3) |

**Table 12 Selected Bond Angles for POBC (grown in DCM/Ether)**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| P28 | Cu1 | P8 | 117.95(2) | C22 | C23 | C24 | 120.4(3) |
| N2 | Cu1 | P8 | 99.49(5) | C23 | C24 | C25 | 120.8(3) |
| N2 | Cu1 | P28 | 125.52(5) | C20 | C25 | N1 | 118.4(2) |
| N2 | Cu1 | N4 | 78.33(7) | C24 | C25 | N1 | 123.7(2) |
| N4 | Cu1 | P8 | 101.41(5) | C24 | C25 | C20 | 118.0(3) |
| N4 | Cu1 | P28 | 125.48(5) | N5 | C26 | C27 | 108.20(19) |
| C32 | P8 | Cu1 | 105.46(7) | C26 | C27 | C28 | 103.49(18) |
| C32 | P8 | C38 | 105.35(10) | N4 | C28 | N3 | 116.81(18) |
| C32 | P8 | C44 | 103.47(10) | N4 | C28 | C27 | 113.12(19) |
| C38 | P8 | Cu1 | 115.81(7) | C27 | C28 | N3 | 130.07(19) |
| C38 | P8 | C44 | 102.18(9) | N3 | C29 | C30 | 107.02(19) |
| C44 | P8 | Cu1 | 122.81(7) | C29 | C30 | C31 | 105.3(2) |
| C55 | P28 | Cu1 | 107.52(7) | N2 | C31 | C30 | 111.4(2) |
| C56 | P28 | Cu1 | 118.08(7) | C33 | C32 | P8 | 120.37(17) |
| C56 | P28 | C55 | 104.04(10) | C33 | C32 | C37 | 119.18(19) |
| C62 | P28 | Cu1 | 119.08(7) | C37 | C32 | P8 | 119.26(16) |
| C62 | P28 | C55 | 105.85(10) | C34 | C33 | C32 | 119.9(2) |
| C62 | P28 | C56 | 100.76(10) | C35 | C34 | C33 | 120.5(2) |
| C19 | O2 | C20 | 115.52(18) | C34 | C35 | C36 | 119.8(2) |
| C50 | O3 | C49 | 116.66(15) | C35 | C36 | C37 | 120.3(2) |
| C11 | N1 | C14 | 118.46(19) | C36 | C37 | C32 | 120.3(2) |
| C25 | N1 | C11 | 117.9(2) | C39 | C38 | P8 | 122.33(17) |
| C25 | N1 | C14 | 117.45(19) | C43 | C38 | P8 | 118.20(16) |
| N3 | N2 | Cu1 | 113.04(13) | C43 | C38 | C39 | 119.4(2) |
| C31 | N2 | Cu1 | 141.47(15) | C40 | C39 | C38 | 119.8(2) |
| C31 | N2 | N3 | 104.81(17) | C41 | C40 | C39 | 120.5(2) |
| N2 | N3 | C28 | 117.65(17) | C42 | C41 | C40 | 120.1(2) |
| C29 | N3 | N2 | 111.48(17) | C41 | C42 | C43 | 119.9(2) |
| C29 | N3 | C28 | 130.81(18) | C38 | C43 | C42 | 120.3(2) |
| N5 | N4 | Cu1 | 141.63(13) | C45 | C44 | P8 | 121.55(16) |
| C28 | N4 | Cu1 | 113.55(14) | C49 | C44 | P8 | 120.80(16) |
| C28 | N4 | N5 | 104.20(16) | C49 | C44 | C45 | 117.64(19) |
| N4 | N5 | C5 | 120.46(16) | C46 | C45 | C44 | 120.8(2) |
| C26 | N5 | N4 | 110.98(17) | C47 | C46 | C45 | 120.5(2) |
| C26 | N5 | C5 | 128.54(18) | C46 | C47 | C48 | 120.0(2) |
| O1 | C1 | C2 | 120.40(19) | C47 | C48 | C49 | 119.3(2) |

## Thermodynamics Analysis

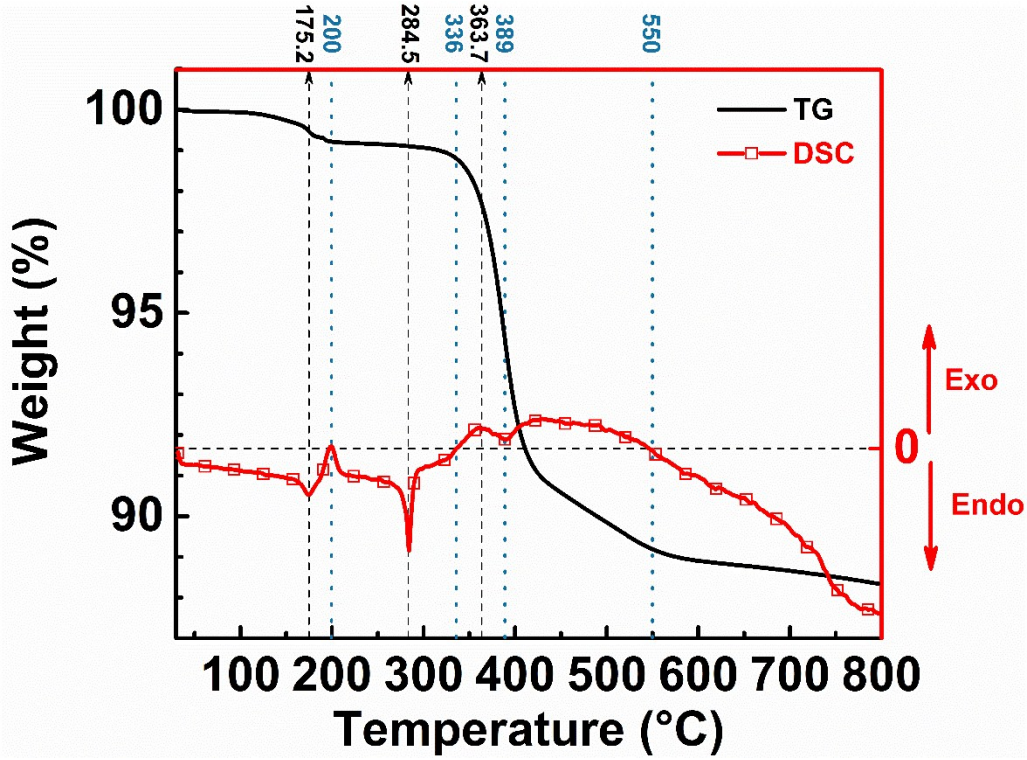



**Fig. S11** Thermogravimetry and Differential Scanning Calorimeter Plot for POBC. The solvent adsorbed in the sample continuously diffused before 200°C. Then the sample began to diffuse and completely liquidified at 284.5°C. The sample decomposed at around 336°C. Further decomposition occurred at c.a. 389°C. The whole decomposition proceeded until the temperature reached 550°C or so. The remnant Selected the sample gasified with the heating afterward.

**Photophysical Property**

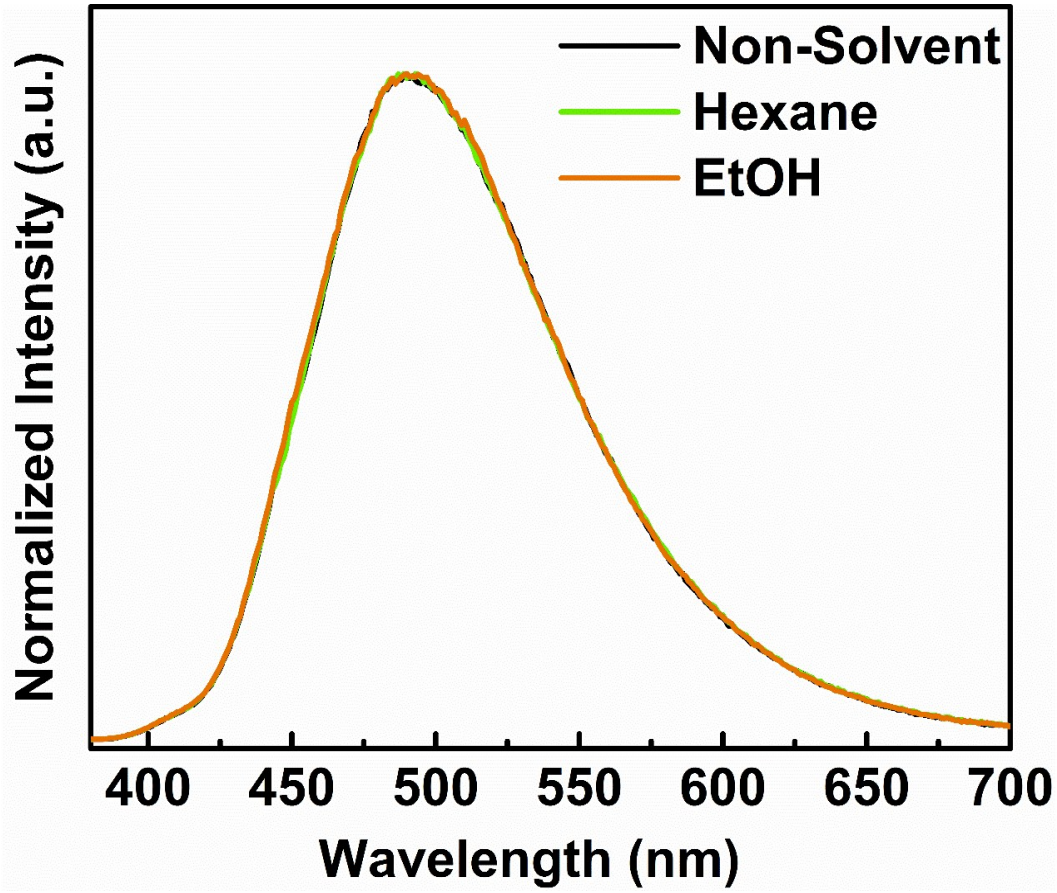



**Fig. S12 Photoluminescence spectra of OBC crystal without fumed and after fumed by hexane and ethanol.**

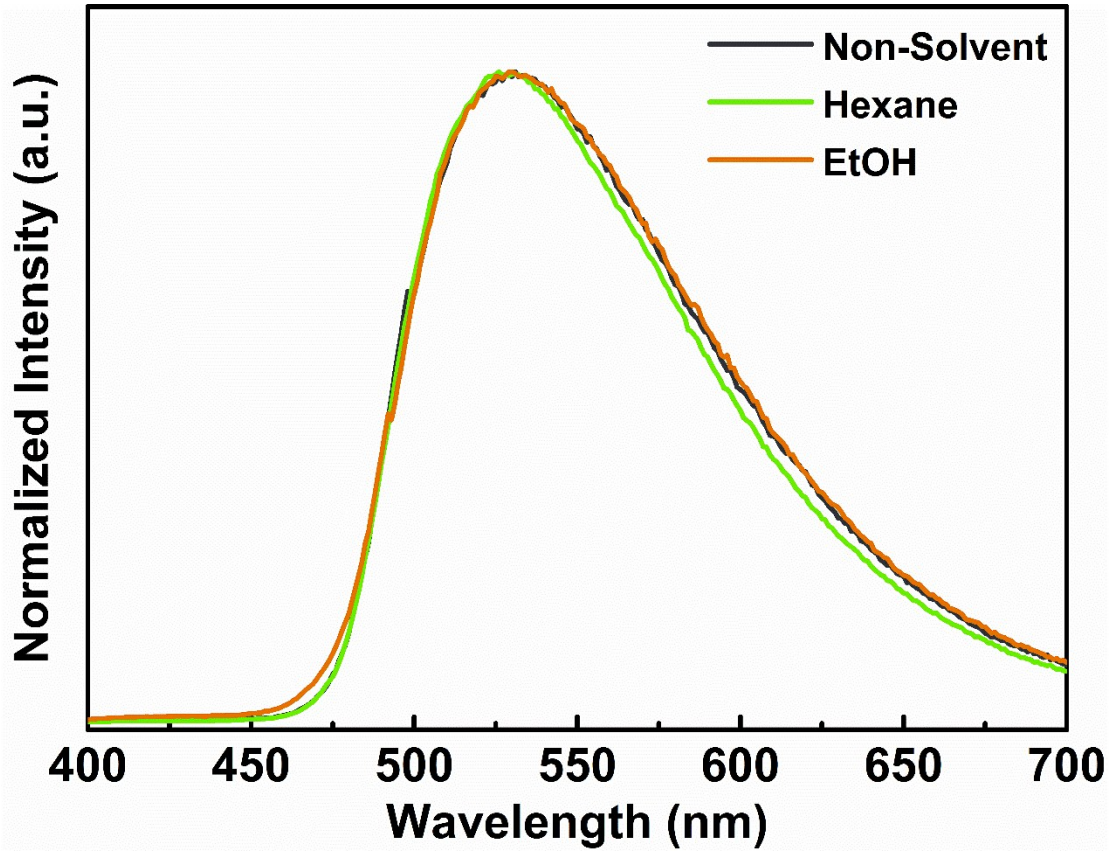



**Fig. S13 Photoluminescence spectra of POB crystal without fumed and after fumed by hexane and ethanol.**

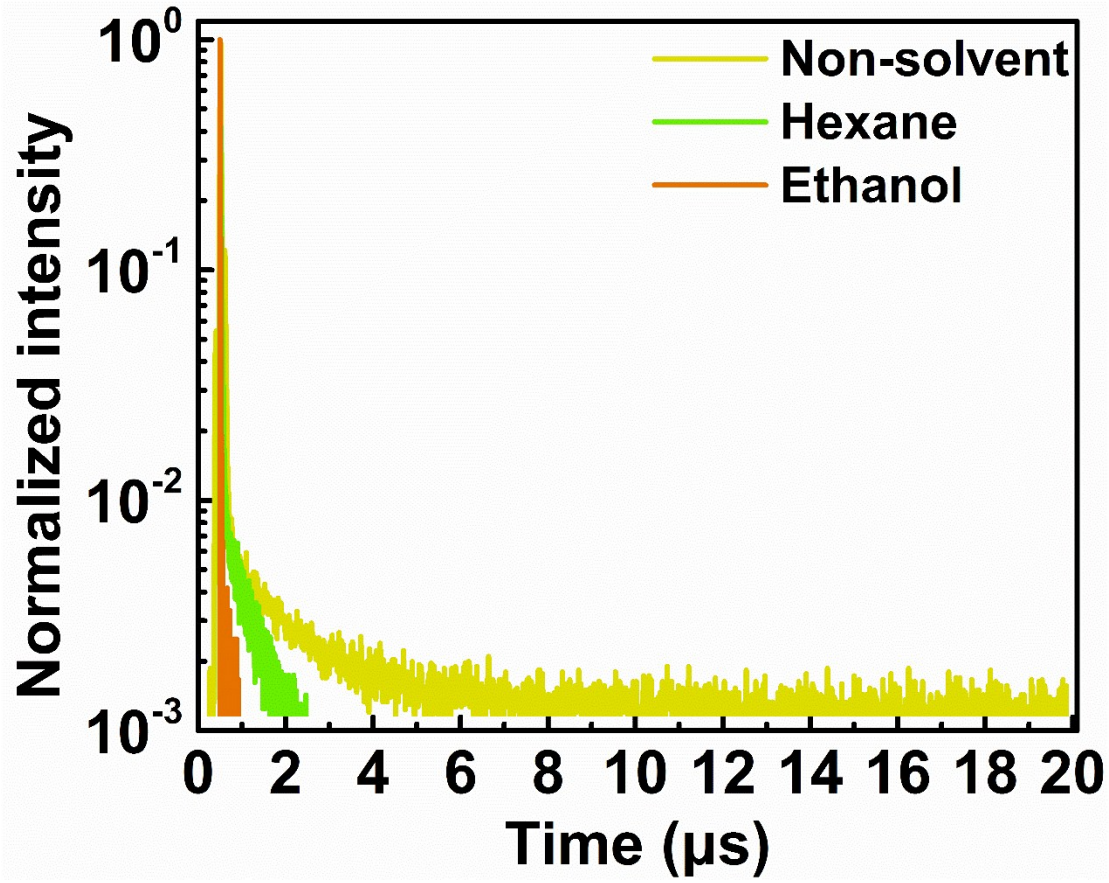



**Fig. S14 Decay Spectra of dry sample, sample immersed in hexane and ethanol, respectively.**

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