# **Electronic supplementary information**

for

Iridium(III) complexes with dithieno[3,2-b:2',3'-d] phosphole oxide group and their high optical power limiting performances  $\dagger$ 

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#### Synthesis of 3,3',5,5'-tetrabromo-2,2'-bithiophene.

Bromine (5.34 mL) was added dropwise to a solution of 2,2'-bithiophene (3.5 g, 21.08 mmol) in acetic acid (18 mL) and chloroform (40 mL) at 0 °C in 0.5 h. The reaction mixture was then warmed to room temperature and stirred for 1 h, and then warmed to 60 °C for 2 h. then the mixture was poured into 1 L of ice-cooled methanol. The light green solid was collected with filtration (9.34 g, 92%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm) 7.05 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm) 132.93, 129.49, 114.79, 112.07.

#### Synthesis of 3,3'-dibromo-2,2'-bithiophene

To a vigorously stirred solution of 3,3',5,5'-tetrabromobithiophene (6.6 g, 1.37 mmol) in ethanol (33.0 mL), water (2.7 mL), acetic acid (8.0 mL) and hydrochloric acid (3.0 M, 2drops) at reflux was added zinc dust (3.0 g, 46 mmol) in 10 portions over 30 min. The reaction mixture was heated to reflux for 3 h. after water quenching, the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. Then the organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and removed under vacuum to obtain yellowish solid. The crude product was purified by silica gel column using petroleum ether as eluent to give the product as a white crystalline solid (3.4 g, 77%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.41 (d, *J* = 5.6 Hz, 2H), 7.09 (d, *J* = 5.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 130.78, 128.84, 127.50, 112.60.

## Dithieno[3,2-b:2',3'-d]phosphole oxide

Under N<sub>2</sub> atmosphere, to the solution of 3,4-dibromo-2,3-bithiophene (1.0 g, 3.08 mmol) in THF was added *n*-BuLi (0.42 mL, 2.5 M in hexane) dropwise slowly at -78 °C. After addition, the reaction mixture was allowed to stir for 0.5 h at this temperature. Then, chlorodiphenylphosphine (2.5 mL) was added to the reaction mixture. The reaction mixture was allowed to warm to room temperature slowly and kept stirring for 1 h. After adding  $H_2O_2$  (0.5 mL), the reaction mixture was extracted with  $CH_2Cl_2$ .

The organic phase was dried over anhydrous MgSO<sub>4</sub> and solvent was removed under vacuum. The residue was chromatographed on a silica column using ethyl acetate and CH<sub>2</sub>Cl<sub>2</sub> (1:1, v/v) as eluent to obtain the product as white solid (0.2 g, 33%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.76-7.72 (m, 2H), 7.54 (td, J = 7.4, 1.2 Hz, 1H), 7.45-7.40 (m, 2H), 7.29 (dd, J = 4.9, 3.3 Hz, 2H), 7.15 (dd, J = 4.9, 2.3 Hz, 2H); <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): 18.62;

## 2-bromodithieno[3,2-*b*:2',3'-*d*]phosphole oxide

To a solution of dithieno[3,2-*b*:2',3'-*d*]phosphole oxide in DMF was added N-bronobutanimided in 6 portions over 30 min under vigorously stirring at 0 °C Then the mixture was allowed to warm to room temperature. Two hours later, the resulting solution was poured into water and extracted with DCM three times. the organic phase was removed under vacuum to get solid residue which was subjected to silica-gel column chromatography using appropriate eluent ethyl acetate and CH<sub>2</sub>Cl<sub>2</sub> (1:1, v/v) to get the product (0.4 g, yield 39%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.74-7.69 (m, 2H), 7.56 (td, *J* = 7.4, 1.2 Hz, 1H), 7.47-7.42 (m, 2H), 7.32 (dd, *J* = 4.9, 3.3 Hz, 1H), 7.16 (dd, *J* = 4.9, 2.3 Hz, 1H), 7.12 (d, *J* = 2.5 Hz, 1H); <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 18.56.

## L-T

Under N<sub>2</sub> atmosphere, 2-bromopyridine (0.6 g, 3.80 mmol), 4-(diphenylamino)phenylboronic acid (1.32 g, 4.56 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.22 g, 0.19 mmol) were added to the mixture of toluene (15 mL) and 2 M Na<sub>2</sub>CO<sub>3</sub> (15 mL). The reaction mixture was heated to 110 °C with vigorous stirring for 24 h. After cooling to room temperature, water (50 mL) was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> ( $3 \times 50$  mL). Collected organic phase was dried over anhydrous MgSO<sub>4</sub> and solvent was removed under vacuum. The residue was chromatographed on a silica column using petroleum ether (60-90 °C) and CH<sub>2</sub>Cl<sub>2</sub> (1:5, v/v) as eluent to obtain the product as pale-yellow solid (1.11 g, 91%). <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.65 (d, *J* = 4.4 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.74-7.65 (m, 2H), 7.30-7.25 (m, 4H), 7.19-7.13 (m, 7H), 7.05 (t, *J* = 7.2 Hz, 2H).

L-C

Under N<sub>2</sub> atmosphere, 2-bromopyridine (0.3 g, 1.90 mmol), 4-(9*H*-carbazol-9-yl)phenylboronic acid (0.65 g, 2.28 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.11 g, 0.09 mmol) were added to the mixture of toluene (10 mL) and 2 M Na<sub>2</sub>CO<sub>3</sub> (10 mL). The reaction mixture was heated to 110 °C with vigorous stirring for 24 h. After cooling to room temperature, water (30 mL) was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL). Collected organic phase was dried over anhydrous MgSO<sub>4</sub> and solvent was removed under vacuum. The residue was chromatographed on a silica column using petroleum ether (60-90 °C) and CH<sub>2</sub>Cl<sub>2</sub> (1:3, v/v) as eluent to obtain the product as pale-yellow solid (0.55 g, 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.76 (d, *J* = 4.8 Hz, 1H), 8.25-8.22 (m, 2H), 8.16 (d, *J* = 7.7 Hz, 2H), 7.85-7.80 (m, 2H), 7.71-7.67 (m, 2H), 7.48 (t, *J* = 8.2 Hz, 2H), 7.45-7.41 (m, 2H), 7.32-7.28 (m, 3H).

Compound	P-Ir-C					
CCDC	1976155					
Formula	$C_{48}H_{34}IrN_3O_3PS_2$					
Formula weight	1094.42					
Temperature (K)	296.15					
Crystal system	triclinic					
Space group	<i>P</i> -1					
<i>a</i> (Å)	11.473(9)					
<i>b</i> (Å)	12.935(10)					
<i>c</i> (Å)	16.291(13)					
α (°)	68.059(10)					
$\beta$ (°)	74.282(10)					
γ (°)	84.609(10)					
Volume (Å <sup>3</sup> )	2159(3)					
Ζ	2					
$D_{calcd}(g/cm^3)$	1.684					
$\mu$ (mm <sup>-1</sup> )	3.459					
F(000)	1084.0					
θ range (°)	1.697-27.112					
Number of reflections collected	6749					
Number of unique reflections	9011					
R <sub>int</sub>	0.0792					
Number of parameters	552					
$R1, wR2 [I > 2.0s (I)]^{a}$	R1 = 0.0598, $wR2 = 0.1391$					
R1, $wR2$ (all data)	R1 = 0.0893, $wR2 = 0.1580$					
Goodness-of-fit on <i>F</i> <sup>2 <i>b</i></sup>	1.011					
${}^{a}R1 = \Sigma   F_{0}  -  F_{c}   / \Sigma  F_{0} .  wR2 = \{ \Sigma [w(F_{0}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{0}^{2})^{2}] \}^{1/2}.  {}^{b}GOF = [(\Sigma w F_{0}  - E_{0})^{2}] / \Sigma [w(F_{0}^{2})^{2}] + E_{0} / \Sigma  W(F_{0})^{2}  + E_{0} / \Sigma  W(F_{0})^{$						
$ F_{\rm c} )^2/(N_{\rm obs}-N_{\rm param})]^{1/2}$ .						

 Table S1 Crystal and Data Parameters for Structure of P -Ir-C

Bond angles (°)			Bond lengths (Å)				
O(2)-Ir(1)-O(3)	88.7(2)	C(33)-S(2)-C(36)	92.3(5)	Ir(1)-O(2)	2.131(5)	N (1)-C(13)	1.454(10)
N(2)-Ir(1)-O(2)	83.3(2)	O(1)-P(1)-C(31)	119.1(4)	Ir(1)-O(3)	2.152(5)	N (2)-C(19)	1.384(11)
N(2)-Ir(1)-O(3)	95.3(2)	O(1)-P(1)-C(34)	115.9(4)	Ir(1)-N(2)	2.036(7)	N (2)-C(23)	1.364(10)
N(2)-Ir(1)-N(3)	175.0(2)	O(1)-P(1)-C(37)	113.1(4)	Ir(1)-N(3)	2.053(7)	N (3)-C(28)	1.369(9)
N(3)-Ir(1)-O(2)	95.0(2)	C(34)-P(1)-C(31)	92.4(4)	Ir(1)-C(15)	1.996(8)		
N(3)-Ir(1)-O(3)	89.4(2)	C(34)-P(1)-C(37)	105.5(4)	Ir(1)-C(30)	2.006(7)		
C(15)-Ir(1)-O(2)	92.2(3)	C(37)-P(1)-C(31)	108.4(4)	S(1)-C(29)	1.996(8)		
C(15)-Ir(1)-N(2)	80.9(3)	C(44)-0(2)-Ir(1)	125.3(5)	S(1)-C(32)	1.724(8)		
C(15)-Ir(1)-N(3)	94.5(3)	C(6)-N(1)-C(13)	125.8(7)	P(1)-O(1)	1.487(6)		
C(15)-Ir(1)-C(30)	88.4(3)	C(12)-N(1)-C(6)	108.3(7)	P(1)-C(31)	1.826(8)		
C(30)-Ir(1)-O(2)	175.4(3)	C(12)-N(1)-C(13)	125.9(7)	P(1)-C(34)	1.798(8)		
C(30)-Ir(1)-O(3)	91.1(2)	C(23)-N(2)-C(19)	117.4(7)	P(1)-C(37)	1.819(9)		
C(30)-Ir(1)-N(2)	101.2(3)	C(24)-N(3)-C(28)	118.6(7)	O(2)-C(44)	1.274(9)		
C(30)-Ir(1)-N(3)	80.4(3)			N(1)-C(6)	1.402(10)		
C(32)-S(1)-C(29)	90.0(4)			N(1)-C(12)	1.398 (10)		

Table S2 Selected structural parameters of P-Ir-C







(b) <sup>31</sup>P NMR spectrum of **P-Ir-P** 



(c) <sup>1</sup>H NMR spectrum of **P-Ir-T** 



(d)<sup>31</sup>P NMR spectrum of **P-Ir-T** 



(f)<sup>31</sup>P NMR spectrum of **P-Ir-C** 

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Figure S1. NMR spectra for the unsymmetrical iridium(III) complexes.



Figure S2. Z-scan measurement setup.



Figure S3. Theoretical fitting Z-scan result with RSA mechanism.



Figure S4. Jablonski diagram of the RSA process.