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# Asymmetric Boron-Cored Aggregation-Induced Emission Luminogen with Multiple Functions Synthesized through Stepwise Conversion from a Symmetric Ligand

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**Table of Contents Entry** 



#### ABSTRACT

Multi-function luminogens have emerged as promising candidates in high-performance sensor and imaging systems. Concise approaches to the synthesis of such molecules are urgently required both for fundamental research and technological applications. In this study, a new symmetric ligand of di(2-hydroxyphenyl)phthalazine with multiple binding sites around a phthalazine unit was readily synthesized, which could be converted efficiently into an asymmetric luminogen (**OBN-DHPP**) through the formation of oxygen-boron-nitrogen bonding. This molecule has a twistable  $\pi$ -extended backbone with a tetra-coordinated boron core bearing two bulky phenyl groups, giving it abundant optical properties including a large Stokes shift, piezochromism, and aggregation-induced emission enhancement. Importantly, the presence of a free phenolic hydroxyl group in the backbone of **OBN-DHPP** enables the incorporation of various functional moieties into the asymmetric luminogen. As an example, polyethylene glycol (PEG)-modified luminogen (OBN-DHPP-PEG<sub>45</sub>) was synthesized. In the aqueous medium, **OBN-DHPP-PEG**<sub>45</sub> could self-assemble into spherical nanoparticles with low cytotoxicity, excellent emission performance as well as high solubility. The results of flow cytometry and fluorescence microscopy reveal that these nanoparticles could be internalized successfully by HeLa cells, demonstrating their potential application in bioimaging.

### INTRODUCTION

In the past few decades, luminogens containing tetra-coordinated boron centers, such as BODIPY, have been developed extensively for application in organic electronics, sensors, and biological imaging, because of their promising optical and electronic properties.<sup>1–3</sup> When used as an organic emitters, BODIPY and its analogs often exhibit weak emission due to the aggregation-caused quenching effect or severe self-absorption resulting from their small Stokes shifts.<sup>4</sup> For this reason, the formation of boron-cored luminogens with aggregation-induced emission (AIE) moieties is emerging as an efficient strategy for achieving intriguing emission behavior in solid or aggregated states.<sup>5,6</sup> Chujo et al. demonstrated that the boron diiminate core with four phenyl substituent groups **I** (Scheme 1) exhibited crystallization-induced AIE characteristics through the suppression of phenyl ring motion around boron diiminate in its solid-state packing structure.<sup>7</sup> Thus, the development of new boron-cored AIE luminogens (AIEgens) still is highly desirable.



Scheme 1. Typical examples of boron-cored AIE luminogens

Recently, considerable research attention has been paid to the construction of AIEgens with tetra-coordinated boron cores through the incorporation of bulky biphenyl borate moieties into versatile multidentate aromatic ligands.<sup>8–10</sup> The alterable fusion of multiple boron moieties in the main backbones of luminogen molecules has a strong effect on the  $\pi$ -conjugated system of these molecules, enabling the tuning of solid-state packing and optoelectronic properties. For example, Curiel reported ladder-type boron-cored complexes II (Scheme 1) that combined the indolo[3,2b]carbazole unit with biphenyl borate,<sup>8</sup> and its optical and electrochemical properties could be tuned effectively by the number of boron complexations. Recently, we synthesized a dual-boroncored luminogen III (Scheme 1) with a  $C_{2v}$ -symmetric structure that exhibited a large Stokes shift, high AIE activity, and reversible piezochromism, likely due to the condensed donoracceptor-donor skeleton associated with the two bulky boron-cored moieties.<sup>9</sup> Owing to its unique luminescence behaviors, this dual-boron-cored luminogen showed the potential application in biological imaging. However, to meet the requirements of biological imaging, AIEgens require extra modification and have complex synthetic routes that are strongly dependent on the rational design and synthesis of ligands.<sup>11-13</sup> Considering these factors, this study focused on the synthesis of symmetric heteroatom-rich ligands that can be modified with multiple functional moieties in sequence through the formation of steric hindrance at active sites, which was a facile approach to obtaining multi-functionalized boron-cored AIEgens. To the best of our knowledge, the developing of such method for the synthesis of functionalized boron-cored AIEgens is still a challenge.

In this paper, we describe the concise synthesis of a new symmetric ligand, 1,4-di(2hydroxyphenyl) phthalazine (**DHPP**), which has multiple binding sites around a phthalazine unit. Upon complexation with a sterically bulky diphenylboron moiety, a novel asymmetric boron-

cored luminogen (**OBN-DHPP**) was obtained that could be easily modified at the free phenolic hydroxyl group in the molecular backbone. For example, the attachment of a poly(ethylene glycol) (PEG) chain produced the amphiphilic luminogen **OBN-DHPP-PEG**<sub>45</sub>. The as-prepared luminogens had crowded geometric structures and versatile functionality, including piezochromism and AIE activity. In particular, PEG modification produced a luminogen with additional self-assembly behavior and excellent biological imaging properties. **RESULTS AND DISCUSSION** 1 (77%)



MgBr

Scheme 2. Synthesis route of asymmetric boron-cored AIEgen

The synthetic route for the asymmetric boron-cored luminogens **OBN-DHPP** and **OBN-DHPP-PEG**<sub>45</sub> is displayed in **Scheme 2**. First, commercial 1,2-benzenedicarbonyl chloride was reacted with 2-mercaptopyridine by using triethylamine as a catalyst to form 1,2-di(S-(pyridine-2'-yl))benzoylbenzene (1) in a yield of 77%. The key intermediate 1.2-di(2-

methoxyl)benzovlbenzene (2), a vellow solid, was obtained in a vield of 85% through the reaction of 1 with the Grignard reagent of 2-methoxylphenylmagnesium bromide. Subsequently, di(2-hydroxyl)-benzoylbenzene (3) was obtained in upon the reduction of 2 with boron tribromide.<sup>14</sup> Under treatment with hydrazine hydrate, **3** was converted into **DHPP**. Finally, **OBN-DHPP** was obtained through the treatment of **DHPP** with triphenylboron in toluene (yield: 94%). All compounds were fully characterized using <sup>1</sup>H, <sup>13</sup>C NMR, and high-resolution MS. In the <sup>1</sup>H NMR spectrum of **DHPP**, six well-resolved proton signals in aromatic rings indicated the material's  $C_{2v}$  symmetric structure (Figure S1). After DHPP was fused with a biphenylboron moiety, the phenol group signals in the spectrum were separated into two peaks, and the peak corresponding to the fused fragment considerably shifted to the low field compared with that corresponding to the unfused fragment, because of the electron-deficient nature of the boron center.<sup>8</sup> Notably, the dual-boron-cored complex, fusing two biphenyl borate moieties with **DHPP**, could not be prepared by treatment with an excess amount of triphenylboron (>2.0 eq.), suggesting that the dense distribution of nitrogen and oxygen atoms in the backbone of **DHPP** sterically hinders the incorporation of two bulky groups.<sup>15</sup> This unique geometric structure of **DHPP** enables different function groups to be conveniently introduced in sequence. Therefore, the as-prepared luminogen (OBN-DHPP) was further modified at the free phenolic hydroxyl group by coupling a PEG chain through a nucleophilic substitution reaction, forming **OBN**-**DHPP-PEG**<sub>45</sub> (PEG, Mn = 2000).<sup>16</sup> As shown in **Figure S2**, a strong C–O–C signal at  $\delta$  = 3.65 ppm is observed in the <sup>1</sup>H NMR spectrum of **OBN-DHPP-PEG**<sub>45</sub>, which confirms the incorporation of PEG onto OBN-DHPP.<sup>17</sup>

A single crystal of **OBN-DHPP**, which was grown by slowly diffusing *n*-hexane into a chloroform solution containing **OBN-DHPP** at ambient temperature, was studied by using

single-crystal X-ray diffraction (XRD). The top view of the luminogen shows that the middle phthalazine fragment is fused with one of the phenolic rings through the ligating boron core with nitrogen and oxygen atoms to form a psuedo-six-membered ring (Figure 1a). Another phenolic unit linked to the phthalazine ring adopts a twisted conformation, in which the free hydroxyl group is faced to the boron-fused backbone, likely due to the formation of a hydrogen bond with a distance of 2.06 Å between the free hydroxyl group and the nitrogen atom (N2) in the phthalazine unit. The dihedral angles defined by the middle phthalazine unit and two benzene rings are 38.97° (Ph1) and 53.76° (Ph2), respectively (Figure 1b). This difference is caused by the conformation being locked by the B-O covalent bond. Chelated by nitrogen and oxygen atoms, a pseudotetrahedron geometry is observed around the boron core bearing two benzene rings, with the boron atom slightly deviated from the mean plane of the fused backbone. A dihedral angle of 21.85° is defined between the mean plane of the fused phthalazine backbone and the plane consisting of boron, nitrogen, and oxygen atoms. This twisted conformation is resulting from steric congestion upon the fusion of a bulky biphenyl borate moiety with **DHPP**. The lengths of B–O and B–N bonds are 1.49 and 1.66 Å, respectively, coinciding with the covalent and coordination natures of these bonds.<sup>18,19</sup> In the packing diagram (Figure 1c-d), the molecule has a parallel packing motif consisting of staged face-to-face dimers aligned in an edge-to-edge manner in each stacking column, with distances ranging from 3.34 to 3.52 Å between neighboring molecules. A weak  $\pi$ - $\pi$  stacking interaction between two phthalazines with a shortest distance of approximately 3.6 Å is observed in each dimer, which is probably due to steric hindrance of the bulky phenyl substituents on the boron atom.<sup>8,10</sup> In each of the parallel columns, many intermolecular interactions are discovered, such as C-H...O interaction (2.70 Å)

and C–H··· $\pi$  interactions (2.89 and 3.39 Å).<sup>9</sup> This high congestion in the bulk phase of **OBN-DHPP** appears to be favorable for a strong AIE effect.



**Figure 1.** Crystal structures (a, b) and packing diagrams (c, d) of **OBN-DHPP** in the top- and side-view representations, respectively

The optical properties of **DHPP** and **OBN-DHPP** in dichloromethane were investigated using UV–visible (UV-vis) and photoluminescence (PL) spectroscopy. The UV-vis spectrum of **DHPP** contains a set of absorption bands at 253 and 352 nm as well as a shoulder peak at approximately 316 nm, which are assigned to the combined transitions of the phthalazine core and two phenol units. The spectrum of **OBN-DHPP**, formed through fusion of the B(Ph)<sub>2</sub> moiety, contains absorption bands at 262, 326, and 406 nm, which is considerable bathochromic shift (185185.2 cm<sup>-1</sup>) with respect to those of **DHPP** (**Figure 2a**), confirming the formation of an extended  $\pi$ -

Page 9 of 26

conjugated backbone. The broad featureless absorption bands of **OBN-DHPP** reveal substantial conformational isomerization resulting from its rotatable substituents and less rigid backbone. This finding is in agreement with those of previous crystallographic analyses.<sup>10</sup> The absorption peaks at 262 and 326 nm in the UV region are attributed to  $\pi$ - $\pi$ \* transitions of the aromatic backbone. By contrast, the absorption peak at 406 nm probably originates from intramolecular charge transfer from the donor of biphenyl borate moieties to the acceptor of phthalazine parts. The solvatochromic properties of **OBN-DHPP** in different organic solvents were also investigated (**Figure S4**). A moderate hypsochromic shift of the S<sub>0</sub>-S<sub>1</sub> transition is observed with increasing solvent polarity. This blue shift of the main absorption bands suggests that the dipole moment of **OBN-DHPP** is easily polarized in the ground state, with respect to its asymmetric D-A structure.<sup>20</sup>

**DHPP** is discovered to exhibit weak fluorescence emission, probably because of low-lying  $n \rightarrow \pi^*$  transitions from typical phthalazine units.<sup>21</sup> By contrast, **OBN-DHPP**, incorporated a B(Ph)<sub>2</sub> moiety, exhibits green luminescence with an emission maxima ( $\lambda_{em}$ ) at 560 nm in CH<sub>2</sub>Cl<sub>2</sub> (**Figure 2b**). Relative to its absorption spectrum, **OBN-DHPP** has a broad emission profile with a large Stokes shift of 64935.1 cm<sup>-1</sup>, which is caused by its low-rigidity backbone. The low fluorescence quantum yield of **OBN-DHPP** in CH<sub>2</sub>Cl<sub>2</sub>, determined using an integrating sphere, is probably due to the low-rigidity molecular skeleton and rotatable phenyl substituents.<sup>22,23</sup> Moreover, the UV-vis absorption and PL spectra of **OBN-DHPP-PEG**<sub>45</sub> in CH<sub>2</sub>Cl<sub>2</sub> show little differences compared with those of **OBN-DHPP**, indicative of the weak influence of PEG on the conjugated backbone of **OBN-DHPP**. The photophysical properties of **OBN-DHPP** and **OBN-DHPP-PEG**<sub>45</sub> are summarized in **Table 1**.



Figure 2. UV-vis absorption spectra (a) and fluorescence spectra (b) of DHPP and OBN-DHPP

in CH<sub>2</sub>Cl<sub>2</sub> ( $2 \times 10^{-5}$  M).

sample	$\lambda_{abs}^{[a]}$	log ɛ	$\lambda_{em}^{[b]}$	$arPsi_{ m f}^{[{ m c}]}$	SS <sup>[d]</sup>	$\tau_{\mathrm{f}}$	k <sub>r</sub> <sup>[e]</sup>	$k_{nr}^{[f]}$
	[nm]		[nm]	[%]	[cm <sup>-1</sup> ]	[ns]	$[10^7  \text{s}^{-1}]$	$[10^7 \text{ s}^{-1}]$
DHPP	352	4.13	437	-	177647.0	-		
<b>OBN-DHPP</b>	406	3.98	560	3.02	64935.1	2.91	1.04	67.92
OBN-DHPP- PEG <sub>45</sub>	401	-	534	3.15	75188.0	3.66	0.86	26.46
OBN-DHPP- PEG <sub>45</sub> <sup>[g]</sup>	398	-	535	4.98	72992.7	4.79	1.04	19.84

**Table 1.** Photophysical data of the as-prepared compounds

[a] Longest absorption maximum. [b] Emission maximum upon excitation at the longest absorption maximum. [c] Absolute quantum yield determined by using with the integrating sphere. [d] Stokes shift, evaluated from the absorption maxima and emission spectra maxima [e] Radiative rate constant  $k_r = \Phi_{f}/\tau_f$ . [f] Non-radiative rate constant  $k_{nr} = (1-\Phi_f)/\tau_f$ . [g] solvent is water.

The electronic structure of the as-prepared **OBN-DHPP** was further evaluated by performing cyclic voltammetry in CH<sub>3</sub>CN. As illustrated in **Figure 3a**, **OBN-DHPP** exhibits reversible one-

#### The Journal of Organic Chemistry

electron reduction with the redox peak at  $E_1 = -1.33$  V, indicative of the electron-deficient nature of boron-fused phthalazine. An irreversible oxidation peak is observed at  $E_2 = 1.56$  V, which likely results from the substituted phenyl groups attached to boron atoms.<sup>10</sup> On the basis of their onset potential values, the LUMO and HOMO energy levels of **OBN-DHPP** are calculated as -3.01 and -5.90 eV, respectively. Moreover, calculated from the optical band gap (2.68 eV) and HOMO energy level, the LUMO energy level of **OBN-DHPP** is -3.22 eV (**Table S1**).

To gain insights into the optoelectronic structure of **OBN-DHPP**, theoretical calculations were performed using TD-DFT (with the RB3LYP/6-31G (d) level) (**Figure 3b**). The LUMO energy level of **OBN-DHPP** is predominantly localized on the phthalazine backbone, consistent with the electron-deficient nature of diazanaphthalene. The HOMO energy level is mainly distributed over the phenyl substituents attached to the boron atom. Such separation of molecular orbitals between the HOMO and LUMO energy level is caused by steric effect around the boron atom, impeding electron delocalization over the entire skeleton, as illustrated in its crystal structure.<sup>24</sup> In the calculated UV-vis spectrum, the absorption band at 467 nm in **Figure S5** is governed by the electron transition from HOMO to LUMO, which represents the absorption band at 406 nm in experimental result, resulting in a negative solvatochromic effect. Accordingly, the computational HOMO and LUMO energy levels of **OBN-DHPP** are -5.84 and -3.24 eV, respectively, which are consistent with those of experimental results.<sup>25</sup>



**Figure 3.** (a) CV curves for **OBN-DHPP** in CH<sub>3</sub>CN at the concentration of  $1 \times 10^{-3}$  M. (0.1 mol L<sup>-1</sup> n-Bu<sub>4</sub>NPF<sub>6</sub>, at a scan rate of 100 mV s<sup>-1</sup>); (b) Calculated molecular orbitals of **OBN-DHPP**.

Owing to the rotatable phenyl substituents in boron centers and the weak rigidity of the fused backbone, the temperature-dependent fluorescence of **OBN-DHPP** in toluene was evaluated. In comparison with that at room temperature, the fluorescent intensity of **OBN-DHPP** at 77 K is remarkably higher with a blue shift of 34 nm, which can be attributed to reorganization energy at the low temperature through the restriction of geometric relaxation excited-state planarization and the freezing of low-frequency out-of-plane vibration (**Figure S6**).<sup>26,27</sup> The fluorescence properties of **OBN-DHPP** in the aggregated state were also investigated. A series of emission spectra of **OBN-DHPP** in THF/water mixtures with different volumetric ratios of water are shown in **Figure 4a**. In pure THF, the fluorescence spectrum shows a flat line parallel to the abscissa, indicating poor fluorescence. When water is added to the THF solution, the fluorescence intensity increases rapidly with increasing water content, and is the highest at 70% (v/v) water (**Figure 4b, Figure S7**). This AIE phenomenon is due to considerable restriction of intramolecular rotational and vibrational motion of the phenyl ring during aggregation. When the water fraction is higher than 70%, lower fluorescence intensity is obtained, and the emission

maximum is blue-shifted by more than 22 nm. This is probably caused by strong intermolecular interactions in the aggregate state of **OBN-DHPP**, as verified by the aforementioned temperature-dependent fluorescence behavior.<sup>27,28</sup>



**Figure 4.** (a) Fluorescence spectra of **OBN-DHPP**  $(10^{-4} \text{ M})$  in THF/water mixtures with different water fractions; (b) The plot of I/I<sub>0</sub> as a function of water fraction; (c) The solid fluorescence spectra of **OBN-DHPP**; (d) Powder XRD patterns of **OBN-DHPP**.

Notably, it is found that **OBN-DHPP** crystallizes in a monoclinic system with high AIE activity confers its mechanoluminescence ability, according to the previous reports.<sup>29</sup> Under illumination with light at 365 nm, the **OBN-DHPP** powders emit brilliant green light with an emission maximum at  $\lambda_{em} = 503$  nm. After grinding, the emission of the powders moves to yellow light, which could be recovered to green through treatment with CH<sub>2</sub>Cl<sub>2</sub> vapor (**Figure 4c**,

**Figure S8**). This reversible conversion is attributed to the highly tunable intermolecular interactions as well as the strong dipole moment associated with the material's asymmetric D-A structure in **OBN-DHPP**.<sup>30</sup> To investigate the influence of molecular packing on luminescence properties, powder XRD was employed to analyze the aggregation behavior of **OBN-DHPP** before and after grinding. **OBN-DHPP** has an XRD pattern with intense and sharp peaks (**Figure 4d**), indicating its highly crystalline character. Because of weak intermolecular interactions, **OBN-DHPP** could be converted into an amorphous state with weak diffraction peaks through grinding treatment. This alteration of the packing behavior of **OBN-DHPP** is in agreement with the solid luminescence performance detailed previously.<sup>9</sup>



Figure 5. (a) UV-vis absorption and (b) PL spectra of OBN-DHPP-PEG<sub>45</sub> in CH<sub>2</sub>Cl<sub>2</sub> and water.

To assess the biological applicability of the boron-cored AIEgens obtained in this study, the water solubility of **OBN-DHPP** and **OBN-DHPP-PEG**<sub>45</sub> was examined (**Figure S9**). In water, hydrophobic **OBN-DHPP** forms numerous large aggregates, making it unsuitable for biological application as a fluorescent probe.<sup>31</sup> By contrast, **OBN-DHPP-PEG**<sub>45</sub> is amphiphilic and can be highly dispersible in water. As shown in **Figure 5** and **Table 1**, both the UV-vis absorption and PL spectra of **OBN-DHPP-PEG**<sub>45</sub> in aqueous solution are similar to those in dichloromethane.

The favorable fluorescence of **OBN-DHPP-PEG**<sub>45</sub> in water is attributed to its unique AIE properties. To clarify the self-assembly behavior of **OBN-DHPP-PEG**<sub>45</sub>, the size and morphology of **OBN-DHPP-PEG**<sub>45</sub> aggregates in aqueous medium were investigated using dynamic light scattering (DLS) and transmission electron microscopy (TEM). The DLS curve shows a narrow distribution with an average aggregate size of approximately 250 nm (**Figure S9b**). The TEM image in **Figure 6a** indicates the formation of spherical micelles with an average diameter of  $250 \pm 50$  nm, which is consistent with the DLS data. The self-assembly mechanism of **OBN-DHPP-PEG**<sub>45</sub> is further demonstrated in **Figure S9c**.<sup>32</sup> Overall, these results demonstrate that **OBN-DHPP-PEG**<sub>45</sub> is suitable for application in biological imaging.



**Figure 6.** (a) TEM photograph of **OBN-DHPP-PEG**<sub>45</sub> nanoparticles at concentration of 0.5 mg mL-1 in water, inset: self-assembly model of **OBN-DHPP-PEG**<sub>45</sub> nanoparticles; (b) fluorescence images of HeLa cells incubated with **OBN-DHPP-PEG**<sub>45</sub> for 2h.

The *in vitro* cytotoxicity of **OBN-DHPP-PEG**<sub>45</sub> was evaluated using an MTT assay with NIH/3T3 normal cells. After 24 h of incubation, cell viability remains above 90% compared with untreated cells when the concentration of **OBN-DHPP-PEG**<sub>45</sub> is 1 mg mL<sup>-1</sup>, indicating the low

cytotoxicity of **OBN-DHPP-PEG**<sub>45</sub> nanoparticles containing biocompatible PEG shell (**Figure S10**). According to the high evaluation of AIE properties, biocompatibility and stability, the cellular uptake of **OBN-DHPP-PEG**<sub>45</sub> nanoparticles at 500  $\mu$ g mL<sup>-1</sup> into HeLa cells was evaluated using flow cytometry. Compared with that of non-pretreated cells, the relative geometrical mean fluorescence intensity of **OBN-DHPP-PEG**<sub>45</sub> increases with the prolongation of incubation time, suggesting progressive attachment of the nanoparticles to HeLa cells (**Figure S11**).<sup>33</sup> The endocytosis of these nanoparticles was also determined by using a fluorescence microscope. As shown in **Figure 6b**, strong green fluorescence is observed mainly in the cytoplasmic regions of living cells cultured with **OBN-DHPP-PEG**<sub>45</sub> for 2 h, demonstrating the successful internalization of nanoparticles in HeLa cells. The brightness of the fluorescence in cells is stronger for longer incubation times (**Figure S12**), which is consistent with the flow cytometry findings. On the basis of the AIE properties and nanometer size of **OBN-DHPP-PEG**<sub>45</sub> in water, biological applications of this AIEgen are currently being investigated.

#### CONCLUSIONS

In this study, we synthesized a new symmetric phthalazine-based ligand with dense multiple binding sites, enabling sequential functionalization through the incorporation of a bulky biphenyl borate and PEG moiety. Two asymmetric boron-cored AIEgens, **OBN-DHPP** and **OBN-DHPP-PEG**<sub>45</sub>, were concisely converted. The as-prepared **OBN-DHPP** exhibits an extended  $\pi$ conjugated D-A structure, which is associated with its congested geometric structures. This unique structure endow the **OBN-DHPP** with multiple functions, including large Stokes shift, piezochromism, and AIE property. In the case of **OBN-DHPP-PEG**<sub>45</sub>, self-assembled nanoparticles in water exhibit good fluorescence performance and low cytotoxicity. Through incubating **OBN-DHPP-PEG**<sub>45</sub> with HeLa cells, the nanoparticles were demonstrated to be

internalized successfully with favorable visualization in the cytoplasm of cells, indicating their suitability for cellular imaging and sensing. This work reveals a new and highly efficient method for concisely synthesizing complex organic luminogens with multiple functions.

#### **EXPERIMENTAL SECTION**

**Materials and Methods.** Phthaloyl dichloride, boron tribromide, 2-bromoanisole, hydrazine hydrate, 2-mercaptopyridine, p-toluenesulfonyl chloride, sodium hydrate, potassium carbonate, sodium chloride, petroleum ether, dichloromethane and all other common solvents were purchased from Adamas-beta Reagent. Triphenylboron, magnesium and poly(ethylene glycol) were purchased from Acros. Triethylamine and dichloromethane were distilled from CaH<sub>2</sub> under nitrogen gas. Tetrahydrofuran was refluxed over sodium wires and benzophenone until anhydride and then distilled to use immediately. All reactions were carried out under a nitrogen atmosphere and performed using Schlenk techniques.

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded on a Mercury Plus 400 (400 MHz for proton, 100 MHz for carbon) spectrometer with tetramethylsilane as the internal reference using CDCl<sub>3</sub> as solvent in all cases. Melting points were taken on a WRS-2A melting point apparatus. Mass spectrometry was measured by an Thermo Scientific Q Exactive Focus Mass spectrometer. Ultraviolet-visible (UV-Vis) spectra were recorded on a HITACHI U-4100 Spectrophotometer. Fluorescence spectroscopy (PL) spectra were obtained with a FluoroMax-4 spectrophotometer. Fluorescent quantum yield ( $\Phi$ ) and Time-resolved fluorescence spectra were recorded on a PTI-QM/TM/IM steady-state & time-resolved fluorescence spectrofluorometer (USA/CAN Photon technology international Int.) by using the time-correlated single-photon counting (TCSPC) technique. Cyclic voltammetry (CV) was performed on a Chenhua 650D electrochemical analyzer in anhydrous CH<sub>3</sub>CN containing recrystallized tetra-n-butyl-

ammoniumhexa fluorophosphate (TBAPF<sub>6</sub>, 0.1M) as supporting electrolyte at 298 K. A conventional three electrode cell was used with a platinum working electrode (surface area of 0.3 mm<sup>2</sup>) and a platinum wire as the counter electrode. The Pt working electrode was routinely polished with a polishing alumina suspension and rinsed with acetone before use. The measured potentials were recorded with respect to Ag/AgCl reference electrode. All electrochemical measurements were carried out under an atmospheric pressure of nitrogen. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Paragon 1000 instrument by KBr sample holder method. Transmission electron microscopy (TEM) studies were performed with a JEOL 2010 instrument at a voltage of 200 kV. Samples were prepared by drop-casting micelle solutions onto carbon-coated copper grids, and then air-drying at room temperature before measurement. Dynamic light scattering (DLS) measurements were performed with a Malvern Zetasizer Nano S apparatus (Malvern Instruments Ltd) equipped with a 4.0 mW He-Ne laser operating at 633 nm. All samples were measured at room temperature and a scattering angle of 173°.

#### Synthetic procedures

Synthesis of 1,2-di(S-(pyridine-2'-yl))benzoylbenzene (1). The mixture of 2-mercaptopyridine (7 g, 63 mmol) and triethylamine (10 mL, 72.14 mmol) was dissolved in THF (80 mL) under the protection of nitrogen. The mixture was cooled in ice-water bath for 20 min, then, a solution of phthaloyl dichloride (6 g, 29.55 mmol) in THF solution (20 mL) was quickly added. The reaction was quenched instantly with 1% HCl (100 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic fractions were washed with water until neutrality, dried over MgSO<sub>4</sub> and recrystallized from Et<sub>2</sub>O. The product was obtained as white solid (8.1 g, 77%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.64 (m, *J* = 7.8 Hz, 2H; Py-H), 7.89 (m, 2H; Py-H), 7.78 (m, 4H; Ar-H), 7.66 (m, 2H; Py-H),

7.31 (m, 2H; Py-H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  190.3, 151.4, 150.4, 137.4, 136.7, 132.0, 131.5, 128.8, 123.8. mp = 78-85.7 °C. HRMS (ESI, m/z) calcd for C<sub>28</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> [M + H]<sup>+</sup> 353.0413; Found 353.0399.

Synthesis of 1,2-di(2-methoxyl)benzoylbenzene (2). A solution of 2-bromoanisole (465 mg, 2.5 mmol) in THF (10 mL) was slowly added to a mixture of iodine activated magnesium (70 mg, 2.92 mmol) in THF (5 mL) to form the Grignard reagent in 5 h at 60 °C. Afterwards, the cold reagent was slowly added to a flask containing compound 1 (352 mg, 1.0 mmol) in absolute THF (50 mL) at 0 °C and stirred overnight. The suspension became brown gradually. Then, the reaction was quenched with 10% HCl (100 mL). After adding dichloromethane, the organic phase was washed with NaOH aqueous solution and water, and the dichloromethane was removed under reduced pressure, the solid was collected and purified by silica-gel column chromatography (dichloromethane: petroleum ether = 1:1, v/v) to give compound 2 as a yellow solid powder (294 mg) in yield of 85%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.50 (t, *J* = 3.4 Hz, 4H), 7.37 (dd, *J* = 3.2 Hz, 5.8 Hz, 4H), 6.88 (dd, *J* = 3.2 Hz, 5.8 Hz, 4H), 3.63 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  196.0, 158.8, 141.2, 135.0, 133.5, 131.5, 130.4, 129.3, 127.9, 120.4, 112.0, 55.8. mp = 125.4-136.8 °C. HRMS (ESI, m/z) calcd for C<sub>22</sub>H<sub>19</sub>O<sub>4</sub> [M + H]<sup>+</sup> 347.1278; Found 347.1267.

**Synthesis of di(2-hydroxyl)benzoylbenzene (3)**. Under the protection of nitrogen, compound **2** (0.38 g, 1.1 mmol) was well dissolved in dichloromethane (10 mL) at 0 °C, the mixture of boron tribromide (0.84 mL, 9 mmol) and dichloromethane (10 mL) was added dropwise under stirring. The reaction temperature was heated to room temperature for overnight. Then, the reaction was quenched with water, the obtained organic phase was collected and concentrated under reduced pressure. The solid was purified by silica-gel column chromatography with dichloromethane: to

give compound **3** as a white solid powder (0.3 g) in yield of 75%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  11.63 (s, 2H, OH), 7.64 (m, 4H; Ar-H), 7.49 (t, *J* = 7.6 Hz, 4H; Ar-H), 7.02 (d, *J* = 8.8 Hz, 2H; Ar-H), 6.84 (dd, *J* = 1.2 Hz, 2H; Ar-H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  201.5, 163.2, 138.9, 137.0, 133.4, 130.4, 129.8, 119.1, 118.6. mp = 156.6-171.7 °C. HRMS (ESI, m/z) calcd for C<sub>20</sub>H<sub>15</sub>O<sub>4</sub> [M + H]<sup>+</sup> 319.0965; Found 319.0955.

Synthesis of 1,4-di(2-hydroxyphenyl) phthalazine (DHPP). A suspension of compound 3 (1.4 g, 4.7 mmol) and hydrazine hydrate (0.24 mL, 5 mmol) in ethanol (30 mL) was stirred for 48 h at 75 °C. After reaction, the ethanol was removed by filtration, and the precipitate was washed with ethanol three time, the product was obtained as pale yellow solid (1.35 g) in yield of 80.3%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  11.39 (s, 2H, OH), 8.48 (dd, *J* = 3.6 Hz, 3.2 Hz, 2H; Ar-H), 7.98 (dd, *J* = 3.2 Hz, 3.2 Hz, 2H; Ar-H), 7.76 (d, *J* = 8.0 Hz, 2H; Ar-H), 7.48 (t, *J* = 8.4 Hz, 2H; Ar-H), 7.26 (d, *J* = 8.0 Hz, 2H; Ar-H), 7.10 (t, *J* = 8.0 Hz, 2H; Ar-H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  201.5, 163.2, 138.9, 137.0, 133.4, 130.4, 129.8, 119.1, 118.6. mp > 230.5 °C. HRMS (ESI, m/z) calcd for C<sub>20</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub> [M + H]<sup>+</sup> 315.1128; Found 315.1117.

Synthesis of diphenylboron-fused di(2-hydroxyphenyl) phthalazine (OBN-DHPP). A mixture of DHPP (314 mg, 1 mmol) and triphenylboron (484 mg, 2 mmol) was dissolved in dried toluene (50 mL). The mixture solution was heated to reflux at 110 °C for 24 hour under nitrogen. After cooling to room temperature, toluene was removed under reduced pressure, the solid was collected and washed with petroleum ether for four times to give **OBN-DHPP** (455 mg) as a yellow solid powder in yield of 94%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.72 (d, *J* = 9.6 Hz; 1H, Ar-H), 8.42 (d, *J* = 9.6 Hz; 1H, Ar-H), 8.35 (s, 1H; OH), 8.11 (d, *J* = 9.6 Hz; 2H, Ar-H), 7.76 (d, *J* = 9.6 Hz, 1H; Ar-H), 7.66 (d, *J* = 8.0 Hz, 1H; Ar-H), 7.58 (t, *J* = 8.0 Hz, 1H; Ar-H), 7.50-7.42 (m, 6H; Ar-H), 7.28-7.23 (m, 6H; Ar-H), 7.18-6.97 (m, 3H; Ar-H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

δ 162.8, 157.1, 156.2, 150.8, 135.3, 134.9, 133.9, 133.3, 132.7, 131.5, 130.6, 128.2, 128.0, 127.3, 127.2, 126.8, 126.5, 121.8, 119.6, 119.5, 119.4, 117.1, 116.7. mp > 161.7 °C. HRMS (ESI, m/z) calcd for C<sub>32</sub>H<sub>22</sub>BN<sub>2</sub>O<sub>2</sub> [M - H]<sup>-</sup>477.1769; Found 477.1778.

Synthesis of OBN-DHPP-PEG<sub>45</sub>.<sup>16</sup> A mixture of OBN-DHPP (100 mg, 0.21 mmol), PEG-OTs (680 mg, 0.32 mmol) and excess potassium carbonate was dissolved in dried acetonitrile (80 mL) with the protection of nitrogen. The mixture solution was heated to reflux for 24 hour under nitrogen. After cooling to room temperature, water and dichloromethane were added into solution, the organic phase was washed with deionized water several times to remove unreacted PEG, and dried under a vacuum. The final product was obtained as pale yellow solid in yield of 82%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.64 (d, *J* = 9.6 Hz; 1H, Ar-H), 8.42 (d, *J* = 9.0 Hz, 1H, Ar-H), 8.08 (br, 1H, Ar-H), 7.98-7.72 (m, 6H, Ar-H), 7.57-7.30 (m, 6H, Ar-H), 7.21-7.05 (m, 6H, Ar-H), 6.96 (t, *J* = 8.0 Hz, 1H; Ar-H), 6.96 (t, *J* = 9.0 Hz, 1H, Ar-H), 7.31-7.05 (m, 6H, Ar-H); 3.81-3.46 (m, 88H, OCH<sub>2</sub>CH<sub>2</sub>) 3.37 (s, 3H, OCH<sub>3</sub>).

#### ASSOCIATED CONTENT

#### **Supporting Information**

Biological experimental information, <sup>1</sup>H/<sup>13</sup>C NMR spectra, HRMS Spectra, FTIR Spectra, UVvis spectra, fluorescence spectra, and Single-crystal X-ray diffraction data for **OBN-DHPP** (CIF). These materials are available free of charge via the Internet at <u>http://pubs.acs.org</u>.

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#### Notes

The authors declare no competing financial interest.

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