# Photochemical & Photobiological Sciences

## PAPER



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# Structurally and electronically modulated spin interaction of transient biradicals in two photon-gated stepwise photochromism<sup>†</sup>

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The development of two-photon induced photochromic compounds is important for advanced photoresponsive materials. The utilization of the long-lived transient states or species for two-photon absorption is one of the efficient strategies to realize the advanced photochemical behavior beyond a onephoton photochemical reaction. We have synthesized bi-photochromic compounds composed of two photochromic phenoxyl-imidazolyl radical complex units. The biphotochromic compounds generate two biradical units when the two photochromic units absorb photons with a stepwise manner. The interaction between the two biradicals through the central bridging phenyl ring is the key feature to control the stepwise photochromic reaction. Here, we introduced aromatic spacers in order to modulate the distance and the dihedral angle between the biradical units. The color and the rate of the thermal back reaction of the stepwise photochromism can be regulated by the control of the central bridging part. These results give important insights to develop desirable advanced photoresponsive compounds.

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## Introduction

Organic photoswitchable materials have been studied in various research fields aiming to develop ophthalmic lenses, optical memory media, photomechanical materials and fluorescence switching dyes.<sup>1-6</sup> The use of light as a stimulus for chemical reactions enables us to control photofunctions temporally and spatially. Recently, a basic principle and system based on a synergetic response between molecules and photons have received much attention for the construction of advanced photoresponsive systems.7-11 The utilization of the long-lived transient states or species as an intermediate state for two-photon absorption is an efficient strategy to realize advanced photochemical behavior beyond a one-photon photochemical reaction: the stepwise two-photon photochemical reaction with nonlinear photoresponse.12-17 To achieve multiple photoresponses depending on the intensity and wavelength of excitation light in bichromophoric systems, the mutual electronic and structural couplings between the chromophores is fundamentally required.<sup>11,13</sup>

†Electronic supplementary information (ESI) available: NMR and MS spectroscopy and other experimental data. See DOI: 10.1039/c7pp00420f Recently, we have developed two-photon induced stepwise photoresponsive systems involving two fast-photochromic units, an imidazole dimer or a phenoxyl-imidazolyl radical complex (PIC), in a molecule (Scheme 1).<sup>18–20</sup> The photochemical reactions of PIC derivatives lead to the generation of a





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#### Paper

couple of imidazolyl and phenoxyl radicals with the half-lives in the range of µs to ms. Because these time-scales of the lifetime is suitable for additional photon absorption,<sup>20</sup> the transient biradical species can be expected to behave as the intermediate state for the two-photon absorption process such as the excited triplet state of energy upconversion processes.<sup>15,16</sup> BisPIC, in which two PIC units are combined in a molecule with a phenyl ring, generates two biradical units when both the PIC units absorb photons with a stepwise manner. It means that the bisPIC derivatives undergo two-photon induced photochromic reactions. After the two-photon reaction, a couple of the imidazolyl radicals at the para-position of the central bridging aromatic ring form a para-quinoid (p-quinoid) structure (such as BDPI-2Y)<sup>21,22</sup> through an antiferromagnetic electronic interaction. Therefore, the photochromic properties are nonlinearly regulated, depending on the excitation light intensity because of the drastic change in the electronic structures between the one-photon produced transient biradical (BR) and the two-photon produced quinoid (Q) states (Scheme 1). The electronic structure of Q is mainly dictated by two types of radical-radical interactions at the precursor tetraradical (TR) state: the interaction between the radicals at the para-position of the central aromatic ring (*p*-interaction) and that at the *ortho*-position (*o*-interaction). Therefore, the interaction between the two transient radical units is the key feature to control the stepwise photochromic reaction.

In this study, we developed novel photochromic compounds based on bisPIC to investigate and to regulate the interaction between the two transient biradical units (Fig. 1). The balance of p- and o-interactions determines the stability of the **Q** state and affects the two-photon induced photochromic properties. To modulate the interactions, we introduced a phenylene spacer to the central aromatic ring of **bisPIC** (1 and 2). The relatively large distance and dihedral angle between the two biradical units will reduce the contribution of the p-interaction, leading to the destabilization of the **Q** state. Moreover, we investigated the effect of the aromaticity of the central phenyl ring on the radical-radical interaction through the measurement of the photochromic property of **3**.

# **Fig. 1** Molecular designs of the bisPIC derivatives **1**, **2** and **3** to control the radical–radical interaction of the transient biradicals.

modulation of dihedral angle

long distance

#### Results and discussion

The plausible two-photon induced photochromic reactions of **1–3** are shown in Scheme 2. It was expected that a one-photon absorption by the initial closed ring form produces the transient **BR**, and the further photochemical reaction of **BR** generates **Q**, as similar to our previous reports.<sup>20</sup> Because the relative spatial arrangements between the imidazolyl and phenoxyl radicals are different in **1** and **2**, the expected two-photon products (**Q**) of **1** and **2** have different conjugation paths between the central aromatic rings and the radical units: the closed-shell structures between the two phenoxyl radicals (**1Q**) and that between two imidazolyl radicals (**2Q**), respectively.

Fig. 2 shows the absorption spectra of 1–3 in benzene. The molar extinction coefficient of 1 is almost twice as large as that of PIC. On the other hand, the absorption spectra of 2 and 3 are largely red-shifted as compared to that of PIC. These results indicate the extended  $\pi$ -conjugation between the two imidazole rings through the biphenyl ring in 2 and 3. The imidazole ring and the phenyl ring at the 2-position of the imidazole ring are coplanar and conjugated as revealed by the X-ray crystallography of PIC.<sup>18</sup> On the other hand, the phenoxyl ring is arranged perpendicularly against the imidazole ring, and the imidazole ring is substituted at the *meta*-position against the position where two PIC units are substituted. Therefore, the two imidazole rings of 1 are not involved in the  $\pi$ -conjugation pathway and no shift of the absorption spectrum was observed.

The transient absorption spectra of 1, 2 and 3 upon 355 nm laser irradiation in benzene are shown in Fig. 3a. The broad transient absorption spectra can be assigned to BRs which are generated by the one-photon absorption of 1, 2 and 3 (1BR, 2BR and 3BR, respectively). The transient absorption spectrum of 1 is almost identical to that of PIC, indicating that the biradical and PIC units of 1BR are independent. On the other hand, the transient absorption spectra of 2 and 3 are different from those of both PIC and bisPIC, indicating that the conjugations of 2BR and 3BR are extended over the biradical and PIC units. The slight shift of the absorption spectrum of 3BR would be due to the conjugation through the phenanthrene unit. These transient absorption spectra monotonically decay in the whole visible regions. The rates of the thermal back reaction of the transient BR show first order reaction kinetics (Fig. 3b). The half-lives of transient 1BR, 2BR and 3BR were estimated to be  $5.0 \times 10^2$ ,  $3.6 \times 10^2$  and 16 ns at room temperature, respectively. As described in a previous report,<sup>23</sup> the stabilization of the phenoxyl radical is efficient in reducing the rate of the thermal back reaction more than the stabilization of the imidazolyl radical. According to this insight, the slight deceleration of the thermal back reaction of 1BR, compared with that of 2BR, would be due to the stabilization of the phenoxyl radical by the delocalization of the  $\pi$ -electron over the phenoxyl radical and the other PIC unit. The fast thermal back reaction of **3BR** will be derived from the large steric hindrance between the biradical unit and the phenanthrene unit. To investigate the two-photon induced photochromism of 1 and

o-interactio



Scheme 2 Stepwise photochromic reaction scheme.



Fig. 2 Steady-state absorption spectra of 1, 2, 3 and PIC in benzene at 298 K.

2, the excitation light intensity dependence on the transient absorption spectra was investigated. While significant change in the transient absorption spectra of 1 was not observed depending on the excitation intensity, a new transient absorption band at around 600–650 nm was observed by increasing the excitation light intensity in the photochromism of 2 (Fig. 4). This new transient absorption band can be tentatively assigned to 2Q, which has the *p*-quinoidal structure between the imidazolyl radicals. It was reported that the *p*-quinoidal structure such as BDPI-2Y had the characteristic absorption band at around 600–650 nm because of the interaction between the two imidazolyl radicals leading to the formation of a closed-shell quinoid structure.<sup>21,22</sup> This absorption band



Fig. 3 (a) Transient vis–NIR absorption spectra of 1 (7.2 × 10<sup>-5</sup> M), 2 (1.6 × 10<sup>-5</sup> M) and 3 (1.4 × 10<sup>-5</sup> M) in degassed benzene at 298 K ( $\lambda_{ex.}$  = 355 nm, 2 mJ mm<sup>-2</sup>, pulse width = 5 ns). (b) Time profiles of the transient absorbance at 600 nm in degassed benzene at 298 K. The inset shows the logarithmic plots for the time profiles of the transient absorbance.



**Fig. 4** Dependence of the transient vis–NIR absorption spectra of **2** (1.6 × 10<sup>-5</sup> M) on the excitation light intensity in degassed benzene ( $\lambda_{ex.}$  = 355 nm, pulse width = 5 ns). The spectra were normalized at 700 nm.

of 2Q disappeared with the half-life of  $1.5 \times 10^2$  ns at 298 K (Fig. S38, ESI†). The dependences of the transient absorption spectra of 1 and 2 on the laser excitation intensity indicate that the *p*-interaction is a key feature to modulate the two-photon photochromic properties. That is, the *p*-interaction between the imidazolyl radicals is more efficient in stabilizing the *p*-quinoidal structure, compared with that between the phenoxyl radicals. It is presumably because the five-membered ring of the imidazole ring avoids the steric repulsion with the central biphenyl unit. Therefore, the small dihedral angle between the central biphenyl ring and the adjacent imidazole ring in 2Q is suitable for the efficient conjugation to form the *p*-quinoidal structure. On the other hand, because of the weak

p-interaction in 1TR, the dominant o-interaction would destabilize the *p*-quinoidal structure, leading to the similar electronic structure of the two-photon product of 1 with that of **1BR.** However, the difference in the absorption spectra between 2BR and 2Q is relatively small compared with that of bisPIC,<sup>19</sup> indicating the lower contribution of the *p*-quinoidal structure in 2Q (Scheme 2). It was revealed by Montgomery in 1986 that the bond lengths in the central section of Chichibabin's hydrocarbons are slightly longer than the usual C=C double bond. They concluded that the longer bond length came from the contribution of the biradical character due to the phenylene spacers in Chichibabin's hydrocarbon.<sup>24–26</sup>

To reveal the origin of the less conjugation between the imidazolyl radicals through the central biphenyl ring in 2Q, we synthesized the biphenyl-bridged bis(imidazolyl radical) derivatives R1, R2 and R3 as reference compounds for the transient absorption spectroscopy of 2. The introduction of methyl substituents to the biphenyl unit varies the dihedral angle between the two adjacent phenyl rings, which directly varies the radial-radical interaction between the imidazolyl radicals. Fig. 5 shows the absorption spectra of R1, R2 and R3 in benzene at room temperature. Compound R1 has the absorption maximum at 710 nm, indicating the extended conjugation and the planar quinoidal structure of R1. The absorption bands of R2 and R3 are blue-shifted by the introduction of the methyl groups. This shift clearly indicates that the increase of the dihedral angle between the two central phenyl rings reduces the conjugation between the imidazolyl radicals, leading to the gradual blue shift of the absorption maximum from 710 nm to 590 nm. The increased transient absorption band of 2 after the intense light excitation has the maximum at around 625 nm. Therefore, this result suggests the relatively large dihedral angle between the two central phenyl rings resulting in the weak p-interaction of 2Q. Because the imidazolyl radicals of 2Q also interact with the phenoxyl radical (o-interaction), the central C-C bond of the p-phenylene structure of 2Q would relatively possess a single bond feature. Therefore, the two PIC units can rotate around the central C-C bond and the contribution of the *p*-interaction is relatively small in the 2Q state, compared with planar R1. Since the pla-



Fig. 5 Steady-state absorption spectra of R1, R2 and R3 in benzene at 298 K.



Fig. 6 Transient absorption spectra of 3 at 20 ns after irradiation by a 355 nm (5 ns) laser pulse. The power density was 2.2 mJ mm<sup>-2</sup> and 0.5 mJ mm<sup>-2</sup>.



Scheme 3 Resonance structures of the phenanthrene bridge of 3.

narity of the diphenyl ring strongly affects the interaction between the radicals, we investigated the photochromic property of the phenanthrene derivative 3, which possesses a coplanar arrangement around the central spacer; the increase in the p-interaction is expected. However, the excitation power dependence of the transient absorption spectra was not observed (Fig. 6). Although the absorption band of 3 is slightly shifted by the conjugation through the phenanthrene unit, 3 shows a photochromic reaction upon 355 nm light irradiation as shown in Fig. 3. That is, the excitation energy of 355 nm light is sufficient for the photochromic reaction of 3. The absorption spectrum of 3BR is also similar to that of 2BR, suggesting that the electronic structure of 3BR is similar to that of 2BR. Therefore, the possibility of the quenching of the bond-breaking process of the C-N bonds of 3 and 3BR due to the energy transfer to the phenanthrene unit is excluded. Thus no excitation intensity dependence of the transient absorption spectra of 3 indicates the small difference in the electronic structures between 3BR and 3TR (or 3Q). When the two imidazolyl radicals of 3Q are conjugated through the phenanthrene ring, the phenanthrene ring loses the aromaticity to form the *p*-quinoidal structure. Hence, no change in the transient absorption spectra would be attributable to the less stabilization energy to form the p-quinoidal structure than the aromatic stabilization energy of the phenanthrene ring (Scheme 3). This result clearly suggests that the aromaticity of the central bridging part is one of the key factors controlling the two-photon induced stepwise photochromism.

#### Conclusions

We modulated the radical-radical interaction between the imidazolyl and phenoxyl radicals in the two-photon generated products of bisPIC derivatives by replacing the bridging phenyl View Article Online Paper anthrene unit, The long dis-

ring with a biphenyl and a phenanthrene unit. The long distance between the imidazolyl radicals increases the o-interaction which induces the large dihedral angle of the central two phenyl rings. This significantly decreases the p-interaction and destabilizes the p-quinoidal structure in Q. We also revealed that the configuration of the imidazolyl and phenoxyl radicals modulates the radical-radical interaction; the p-interaction between two imidazolyl radicals is efficient because of the less steric repulsion between the imidazole ring and the central aromatic ring. In addition to the above spatial control of the arrangement of the radicals, the aromaticity of the central phenyl ring determines the preferential interaction of radicals. Therefore, the color and the rate of the thermal back reaction of the stepwise photochromism can be regulated by the control of the central bridging part. These results will give useful insight to design and to develop attractive photoresponsive materials.

### **Experimental section**

#### Laser flash photolysis

Laser flash photolysis experiments were carried out with a TSP-2000 time resolved spectrophotometer (Unisoku). A 10 Hz Q-switched Nd:YAG (Continuum Minilite II) laser with the third harmonic at 355 nm (time duration: 5 ns) was employed for the excitation light. The probe beam from a halogen lamp (OSRAM HLX64623) was irradiated to the sample solution arranged in an orientation perpendicular to the exciting laser beam. The transmitted probe beam was monitored with a photomultiplier tube (Hamamatsu R2949) through a spectrometer (Unisoku MD200) for the transient absorption spectra and the decay profiles of the open-ring isomers of **1**, **2** and **3**. The excitation intensity was estimated by an energy detector (Gentec Electro-Optics QE12LP-S-MB) with an energy monitor (Gentec Electro-Optics MAESTRO). Optical grade solvents were used for all measurements.

#### Synthetic procedure

All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Silica gel 60N, Kanto Chemical Co., Inc.). <sup>1</sup>H NMR spectra were recorded at 400 MHz on a Bruker AVANCE III 400 NanoBay and at 500 MHz on a JEOL JNM-ECP500A. DMSO- $d_6$  and CDCl<sub>3</sub> were used as deuterated solvents. ESI-TOF-MS spectra were recorded on a Bruker micrOTOF II-AGA1 system. FAB-MS spectra were measured by using a JEOL MStation MS700. All glassware was washed with distilled water and dried. Unless otherwise noted, all reagents and reaction solvents were purchased from Tokyo Chemical Industry Co., Ltd, Wako Pure Chemical Industries, Ltd, Sigma-Aldrich Inc. and Kanto Chemical Co., Inc. and were used without further purification.

**4,4'-Dibromo-3,3'-dimethyl-1,1'-biphenyl** (4). 50% aqueous  $H_2SO_4$  (20 mL) was added to *o*-tolidine (3.00 g, 14.1 mmol). 45% aqueous NaNO<sub>2</sub> (3 mL) and CuBr (17.1 g, 118.7 mmol) in

Photochemical & Photobiological Sciences

47% aqueous HBr (39 mL) were added dropwise to the mixture at 0 °C and the mixture was warmed to room temperature. After gently stirring for 2.5 h at 100 °C,  $CH_2Cl_2$  and water were added to the reaction mixture. The crude product was filtered through a Celite pad to remove insoluble solid. The filtrate was extracted with  $CH_2Cl_2$ , and the organic layer was washed with water and brine. The solvent was removed by evaporation. The product was purified by silica gel column chromatography with hexane as an eluent, to give 4 as a white solid (1.17 g, yield: 24%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.57 (d, *J* = 8.0 Hz, 2H), 7.41 (s, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 6H).

4,4'-Dibromo-3,3'-bis(dibromomethyl)-1,1'-biphenyl (5). *N*-Bromosuccinimide (2.78 g, 15.6 mmol) and azobis(isobutyronitrile) (172 mg, 1.05 mmol) were added to 4 (1.10 g, 3.24 mmol) in CCl<sub>4</sub> (22 mL). After stirring for 13 h at 75 °C, the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, succinimide was filtered off, and washed with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The organic layer was washed with water and brine, and passed through a phase separator paper. The solvent was removed by evaporation and the crude mixture was purified by silica gel column chromatography with hexane : CH<sub>2</sub>Cl<sub>2</sub> = 2 : 1 as an eluent, to give 5 as a pale yellow solid (1.69 g, yield: 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.20 (s, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.13 (s, 6H).

**4,4'-Dibromo-[1,1'-biphenyl]-3,3'-dicarbaldehyde** (6). NaHCO<sub>3</sub> (1.78 g, 21.1 mmol) was added to the DMSO solution (20 mL) of **5** (1.66 g, 2.54 mmol). The mixture was stirred for 18 h at 100 °C. After cooling to room temperature, the reaction was quenched with water. The organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with water and brine, and passed through a phase separator paper. The solvent was removed under vacuum to give **6** as a pale yellow solid (775 mg, yield: 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): *δ* 10.42 (s, 2H), 8.14 (s, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H).

4,4"'-Dihydroxy-[1,1':4',1":4",1"'-quaterphenyl]-2',3"-dicarbaldehyde (7). Compound 6 (196 mg, 0.532 mmol) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (544 mg, 2.47 mmol) were dissolved in THF (7.9 mL) and aqueous 1.3 M Na<sub>2</sub>CO<sub>3</sub> (2.2 mL). The mixture was degassed by freeze pump thaw cycles. Tetrakis(triphenylphosphine)palladium(0) (33 mg, 28.3 µmol) was added to the solution and the solution was stirred for 22 h at 85 °C. The reaction mixture was extracted with AcOEt. The organic layer was washed with water and brine, and passed through a phase separator paper. The solvent was removed by evaporation, and the product was purified by silica gel column chromatography (hexane:  $CH_2Cl_2 =$ 1:1) to give 7 as a yellow solid (186 mg, yield: 87%). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  9.98 (s, 2H), 9.82 (s, 2H), 8.18 (s, 2H), 8.13 (d, J = 8.0 Hz, 2H) 7.65 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.4 Hz, 4H), 6.93 (d, J = 8.8 Hz, 4H).

2',3''-Bis(4,5-diphenyl-1*H*-imidazol-2-yl)-[1,1':4',1'':4'',1'''-quaterphenyl]-4,4'''-diol (8). Compound 7 (100 mg, 0.436 mmol), benzil (172 mg, 0.819 mmol) and ammonium acetate (590 mg, 7.65 mmol) in acetic acid (1.7 mL) were stirred for 2 d at 110 °C. The reaction mixture was allowed to cool to room temperature, neutralized by aqueous ammonia and filtered. The crude product was washed with water and  $CH_2Cl_2$  to give **8** as a pale yellow solid (86 mg, yield: 43%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  12.12 (s, 2H), 9.46 (s, 2H), 8.12 (s, 2H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.56–7.19 (m, 26H), 6.75 (d, *J* = 8.6 Hz, 4H); HRMS (ESI-TOF) calcd for  $C_{54}H_{38}N_4O_2$  [M + H]<sup>+</sup>, 775.3068; found, 775.3085.

**Compound 1.** A solution of potassium ferricyanide (1.64 g, 29.3 mmol) and aqueous 0.3 M KOH (20 mL) was added to a solution of **8** (42 mg, 53 µmol) and benzene (22.4 mL). After stirring for 2.5 h at room temperature, the resultant solution was diluted with AcOEt. The organic layer was washed with water and brine. The solvent was evaporated under reduced pressure. The residual solid was suspended in hexane, filtered, and washed with hexane :  $CH_2Cl_2 = 1:1$  to give **1** as a milky white solid (24 mg, yield: 58%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.32 (s, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 4H), 7.44–7.17 (m, 22H), 7.02 (d, *J* = 10 Hz, 2H), 6.26 (d, *J* = 9.6 Hz, 4H); HRMS (ESI-TOF) calcd for  $C_{54}H_{34}N_4O_2$  [M + H]<sup>+</sup>, 771.2755; found, 771.2793 (Scheme 4).

2-Bromo-4-iodo-1-methylbenzene (9). 1N aqueous HCl (34 mL) was added to 3-bromo-4-methylaniline (25 g, 0.134 mmol) in water (34 mL). The mixture was heated to 60 °C and stirred for 1 h. After cooling to 0 °C, 32% aqueous NaNO<sub>2</sub> (21.5 mL) and 50% aqueous KI (23.5 mL) were added dropwise to the mixture at 0 °C. The mixture was vigorously stirred for 30 minutes at 0 °C. After further stirring for 1 h at 60 °C, the mixture was cooled to room temperature and extracted with diethyl ether. The organic layer was washed with aqueous  $Na_2S_2O_3$ , water and brine, passed through a phase separator paper, and the solvent was evaporated under reduced pressure. The product was purified by silica gel column chromatography (hexane) to give 10 as a pale pink liquid (28.6 g, yield: 72%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.86 (s, 1H), 7.51 (d, J = 8.0 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 2.34 (s, 3H).

(3-Bromo-4-methylphenyl)boronic acid (10). To a solution of 9 (500 mg, 1.65 mmol) in dry THF (3.12 mL) was added dropwise a solution of isopropylmagnesium chloride (192 mg, 1.87 mmol) in THF (0.925 mL) at -78 °C. After stirring at -78 °C for 30 minutes, the mixture was warmed slowly to -20 °C and stirred for 1 h. After cooling again to -78 °C, trimethylborate (350 mg, 3.37 mmol) was added dropwise. After warming to 0 °C, the mixture was stirred for 2 h, treated with 1N aqueous HCl (1.46 mL), and extracted with ethyl acetate. The organic layer was washed with water and brine, passed through a phase separator paper, and the solvent was evaporated under vacuum. The residual solid was suspended in hexane, filtered, and washed with hexane to provide 11 as a white solid (273 mg, yield: 75%). <sup>1</sup>H NMR (400 MHz, DMSO $d_6$ ):  $\delta$  8.17 (s, 2H), 7.95 (s, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 2.34 (s, 3H).

**3,3'-Dibromo-4,4'-dimethyl-1,1'-biphenyl (11).** Compound **10** (2.50 g, 11.6 mmol) was dissolved in methanol (30 mL). After the addition of copper(i) chloride (0.058 g, 0.058 mmol), the mixture was stirred for 4 h at room temperature under air. The



Scheme 4 Synthesis of 1.

reaction mixture was filtered and washed with ethyl acetate. The solvent was evaporated under reduced pressure and the crude product was purified by silica gel column chromatography (hexane) to afford **12** as a white solid (1.04 g, yield: 52%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.72 (s, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 6H).

**3,3'-Dibromo-4,4'-bis(dibromomethyl)-1,1'-biphenyl** (12). *N*-Bromosuccinimide (2.26 mg, 12.7 mmol) was added to **11** (900 mg, 2.65 mmol) in CCl<sub>4</sub> (18 mL). Azobis(isobutyronitrile) (150 mg, 0.913 mmol) was added to the solution and the mixture was stirred for 22 h at 75 °C. After cooling to room temperature, the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and filtered to remove succinimide. The organic layer was washed with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, water and brine, and passed through a phase separator paper. The solvent was evaporated under reduced pressure. The product was purified with silica gel column chromatography (hexane) to give **12** as a pale yellow solid (933 mg, yield: 53%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.10 (d, *J* = 8.4 Hz, 2H), 7.69 (s, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.10 (s, 2H).

**3,3'-Dibromo-[1,1'-biphenyl]-4,4'-dicarbaldehyde** (13). NaHCO<sub>3</sub> (840 mg, 10.0 mmol) was added to **12** (800 mg, 1.22 mmol) in DMSO (9.7 mL). The mixture was stirred for 16 h at 100 °C. After cooling to room temperature, water was added to the reaction mixture. The organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with water and brine, passed through a phase separator paper, and evaporated, to give **13** as a milky white solid (1.09 g, yield: 89%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.41 (s, 2H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.89 (s, 2H), 7.67 (d, *J* = 8.0 Hz, 2H).

**4**,4<sup>*'''*-**Dihydroxy-[1,1':3',1<sup>''</sup>:3'',1<sup>'''</sup>-quaterphenyl]-4'',6'-dicarbaldehyde (14).** Compound **13** (150 mg, 0.362 mmol) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (243 mg, 1.10 mmol) were dissolved in THF (5.3 mL) and 1.2 M aqueous</sup> Na<sub>2</sub>CO<sub>3</sub> (1.5 mL). The solution was degassed by freeze pump thaw cycles. Tetrakis(triphenylphosphine)palladium(0) (24 mg, 21 µmol) was added and the mixture was stirred at 75 °C for 17.5 h. The resultant mixture was extracted with AcOEt. The organic layer was washed with water and brine, passed through a phase separator paper, and the solvent was removed under reduced pressure. The product was purified by silica gel column chromatography (hexane : CH<sub>2</sub>Cl<sub>2</sub> = 1 : 1) to give **14** as a pale yellow solid (141 mg, yield: 98%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.93 (s, 2H), 9.78 (s, 2H), 8.00–7.94 (m, 4H), 7.89 (s, 2H), 7.38 (d, *J* = 8.4 Hz, 4H), 6.92 (d, *J* = 8.8 Hz, 4H).

**4**",**6**'-**Bis**(**4**,**5**-**diphenyl-**1*H*-**imidazol-**2-**yl**)-[**1**,**1**':**3**',**1**":**3**",**1**"'-**quaterphenyl**]-**4**,**4**"'-diol (15). Compound **14** (100 mg, 0.253 mmol), benzil (161 mg, 0.766 mmol) and ammonium acetate (599 mg, 7.77 mmol) in acetic acid (1.7 mL) were stirred for 23 h at 110 °C. After cooling to room temperature, the reaction mixture was neutralized by aqueous ammonia and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed by water and brine, and the solvent was evaporated under reduced pressure. The crude product was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub> to give **15** as a pale yellow solid (136 mg, yield: 69%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): *δ* 11.85 (s, 2H), 9.46 (s, 2H), 7.86–7.79 (m, 6H), 7.48 (d, *J* = 7.2 Hz, 4H), 7.39–7.18 (m, 10H), 6.77 (d, *J* = 8.4 Hz, 4H); HRMS (ESI-TOF) calcd for C<sub>54</sub>H<sub>38</sub>N<sub>4</sub>O<sub>2</sub> [M + Na]<sup>+</sup>, 797.2887; found, 797.2909.

**Compound 2.** A solution of potassium ferricyanide (2.02 g, 53 mmol) and 1.2 M aqueous KOH (24 mL) was added to a solution of **15** (50 mg, 500  $\mu$ mol) in benzene (22 mL) and EtOH (6 mL). After stirring for 2 h at room temperature, the resultant mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with water and brine, and the solvent was evaporated under vacuum. The residual solid was suspended in hexane, filtered, and washed with hexane as a yellow solid (46 mg, yield: 71%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  7.98–7.93 (m, 4H), 7.60 (s,

2H), 7.47 (d, J = 7.2 Hz, 4H), 7.43–7.17 (m, 18H), 6.95 (d, J = 9.6 Hz, 4H), 6.23 (d, J = 9.6 Hz, 4H). HRMS (ESI-TOF) calcd for  $C_{54}H_{34}N_4O_2$  [M + H]<sup>+</sup>, 771.2755; found, 771.2768 (Scheme 5).

(2-Bromo-3-methylphenyl)methanol (16). 2-Bromo-3-methylbenzoic acid (3.00 g, 13.9 mmol) was dissolved in dry THF (18 mL). BH<sub>3</sub>-THF (30 mL, 1.0 M in THF) was added dropwise to the reaction mixture and stirred at room temperature for 14 h. The reaction mixture was cooled to 0 °C and the reaction was slowly quenched with MeOH. The solution was poured into 45 mL of saturated aqueous NaHCO<sub>3</sub> and extracted with AcOEt. The organic layer was washed with water and brine, and passed through a phase separator paper. The material was concentrated under reduced pressure to give **16** as a white solid (2.19 g, yield: 75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.36 (d, J = 7.2 Hz, 1H), 7.29 (t, J = 7.7 Hz, 1H), 7.24 (d, J = 7.2 Hz, 1H), 5.41 (t, J = 5.6 Hz 1H), 4.51 (d, J = 5.6 Hz, 2H), 2.36 (s, 3H).

**2-Bromo-3-methylbenzaldehyde** (17). PCC (1.54 g, 7.16 mmol) and a molecular sieve (MS-4A, 5 g) were added to a solution of **16** (1.09 g, 5.21 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (16 mL). The mixture was stirred at room temperature for 2.5 h. Then, MS-4A was filtered off and the crude mixture was purified by silica gel column chromatography with CH<sub>2</sub>Cl<sub>2</sub> as an eluent, to give **17** as a white solid (0.846 g, yield: 82%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.46 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 2.49 (s, 3H).

1,2-Bis(2-bromo-3-methylphenyl)ethane(18). $TiCl_4$ (0.615 mL) was slowly added dropwise to a suspension of zincpowder (0.630 g, 9.63 mmol) and dry THF (21 mL) at roomtemperature. The resulting mixture was refluxed at 70 °C for1 h and cooled to room temperature. The THF solution(2.9 mL) of 17 (1.002 g, 5.03 mmol) was slowly added dropwiseto the resulting mixture at 0 °C. The mixture was refluxed at

75 °C for 15 h and cooled to room temperature. The reaction mixture was then poured into ice-cold 1 M aqueous HCl (15 mL) and extracted with  $CH_2Cl_2$ . The organic layer was washed with brine, passed through a phase separator paper and concentrated under reduced pressure. The residue was purified by recrystallization from MeOH to yield **18** (0.543 g, yield: 59%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.55 (d, *J* = 6.8 Hz, 2H), 7.43 (s, 2H), 7.25–7.17 (m, 4H), 2.45 (s, 6H).

**1,8-Dibromo-2,7-dimethylphenanthrene (19).** Compound **18** (0.604 g, 1.65 mmol) and iodine (0.471 g, 1.87 mmol) were added to toluene (402 mL). The solution was irradiated with a 400 W high pressure Hg-lamp for 9 h. The reaction mixture was diluted with  $CH_2Cl_2$  and washed with sodium dithionite in water. The organic layer was washed with water and concentrated under reduced pressure. The crude product was purified by recrystallization from toluene to give **19** as a yellow crystal (0.404 g, yield: 36%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.52 (d, *J* = 8.8 Hz, 2H), 8.37 (s, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 2.67 (s, 6H).

**3,3'-Dibromo-[1,1'-biphenyl]-4,4'-dicarbaldehyde** (20). The reaction mixture of **20** (0.308 g, 0.845 mmol), NBS (0.308 g, 1.73 mmol) and  $CCl_4$  (2.67 mL) was refluxed at 80 °C for 1.5 h under irradiation with a 100 W high pressure Hg-lamp before adding NBS (0.321 g, 1.80 mmol) and  $CCl_4$  (2 mL). The resulting solution was refluxed at 80 °C for 1.5 h under irradiation with the high pressure mercury lamp and NBS (0.303 g, 1.79 mmol) was added to the solution. The reaction mixture was refluxed for 17.5 h under irradiation, and cooled to room temperature. The product was filtered and washed with water and  $CHCl_3$ . The organic phase was washed with saturated aqueous NaHSO<sub>3</sub>, passed through a phase separator paper and concentrated under reduced pressure. The crude product was washed with hexane to give **20** as a yellow solid (0.264 g, yield:



Scheme 5 Synthesis of 2.

46%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.75 (d, J = 8.8 Hz, 2H), 8.44 (s, 2H), 8.33 (d, J = 8.8 Hz, 2H), 7.47(s, 2H).

**1,8-Dibromophenanthrene-2,7-dicarbaldehyde** (21). To a solution of **20** (50 mg, 72 µmol) in EtOH (3.5 mL) was added a solution of AgNO<sub>3</sub> (68 mg, 400 mmol) in water (0.7 mL), and the mixture was refluxed under a N<sub>2</sub> atmosphere for 1 h at 110 °C. The reaction mixture was allowed to cool to room temperature, filtered to remove AgBr and washed with hot CH<sub>2</sub>Cl<sub>2</sub>. The combined filtrate was washed with water and passed through a phase separator paper. The solvent was removed under reduced pressure to give **21** as a yellow solid (14 mg, yield: 47%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.72 (s, 2H), 8.79 (d, *J* = 8.8 Hz, 2H), 8.64 (s, 2H), 8.21 (d, *J* = 8.8 Hz, 2H).

1,8-Bis(4-hydroxyphenyl)phenanthrene-2,7-dicarbaldehyde (22). Compound 21 (8.9 mg, 23 µmol) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (17 mg, 74 µmol) were dissolved in THF (3 mL). 0.12 M aqueous Na<sub>2</sub>CO<sub>3</sub> (2 mL) was added to the solution and the mixture was degassed by freeze pump thaw cycles. Tetrakis(triphenylphosphine)palladium(0)  $(3.7 \text{ mg}, 3.2 \mu \text{mol})$  was added to the solution and the solution was refluxed at 75 °C for 12 h. The mixture was filtered through a pad of Celite and extracted with AcOEt. The organic layer was washed with water and brine, passed through a phase separator paper, and the solvent was evaporated under reduced pressure. The product was purified by silica gel column chromatography ( $CH_2Cl_2$ : AcOEt = 5:1) to give 22 as a yellow solid (6.9 mg, yield: 73%). <sup>1</sup>H NMR (400 MHz, DMSO $d_6$ ):  $\delta$  9.86–9.85 (m, 4H), 9.16 (d, J = 9.2 Hz, 2H), 8.17 (d, J = 8.4 Hz, 2H), 7.63 (s, 2H), 7.27 (d, J = 8.4 Hz, 4H), 6.97 (d, J = 8.4 Hz, 4H); HRMS (ESI-TOF) calcd for  $C_{28}H_{18}O_4$  [M - H]<sup>-</sup>, 417.1121; found, 417.1134.

**4**,4'-(**2**,7-Bis(**4**,5-diphenyl-1*H*-imidazol-2-yl)phenanthrene-**1**,8-diyl)diphenol (23). Compound 22 (23.7 mg, 56.6 μmol), benzil (60.5 mg, 288 μmol) and ammonium acetate (156 mg, 2.02 mmol) in acetic acid (0.7 mL) were stirred at 110 °C for 21 h. The reaction mixture was allowed to cool to room temperature, neutralized by aqueous ammonia and filtered. The mixture was washed with water and CH<sub>2</sub>Cl<sub>2</sub> to give **23** as a pale yellow solid (28.0 mg, yield: 62%). <sup>1</sup>H NMR (400 MHz, DMSO*d*<sub>6</sub>): δ 11.27 (s, 2H), 9.59 (s, 2H), 9.10 (d, *J* = 9.2 Hz, 2H), 8.22 (d, *J* = 8.4 Hz, 2H), 7.52–7.16 (m, 26H), 6.89 (d, *J* = 8.4 Hz, 4H); HRMS (ESI-TOF) calcd for C<sub>56</sub>H<sub>38</sub>N<sub>4</sub>O<sub>2</sub> [M + H]<sup>+</sup>, 799.3068; found, 799.3092.

**Compound 3.** A solution of potassium ferricyanide (404 mg, 1.23 mmol) and 1.6 M aqueous KOH (4.8 mL) was added to a solution of 23 (10.6 mg, 13.3 µmol) in benzene (5.4 mL). After stirring for 2 h at room temperature, the resultant mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the organic layer was washed with water and brine. The solvent was removed under reduced pressure and the residual solid was suspended in cold CH<sub>2</sub>Cl<sub>2</sub>, filtered, and washed with cold CH<sub>2</sub>Cl<sub>2</sub> to give compound 3 as a yellow solid (62 mg, yield: 63%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.28 (d, *J* = 8.8 Hz, 2H), 8.30 (d, *J* = 8.8 Hz, 2H), 7.57–7.15 (m, 11H), 7.00 (d, *J* = 9.6 Hz, 4H), 6.32 (d, *J* = 10.0 Hz, 4H); HRMS (ESI-TOF) calcd for C<sub>56</sub>H<sub>34</sub>N<sub>4</sub>O<sub>2</sub> [M + H]<sup>+</sup>, 795.2754; found, 795.2793 (Scheme 6).

**4,4'-Bis(4,5-diphenyl-1H-imidazol-2-yl)-1,1'-biphenyl** (24). (1,1'-Biphenyl)-4,4'-dicarbaldehyde (200 mg, 0.95 mmol), benzil (400 mg, 1.90 mmol) and ammonium acetate (1.46 g, 19.0 mmol) in acetic acid (15 mL) were stirred at 110 °C overnight. After cooling to room temperature, the solution was neutralized by aqueous ammonia. The suspension was filtered and the collected solid was washed with ethanol and recrystal-



Scheme 6 Synthesis of 3.

Photochemical & Photobiological Sciences

lized from pyridine to give 24 as a pale yellow solid (229 mg, yield: 40%). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  12.78 (s, 2H), 8.20 (d, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 4H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.36 (s, 2H), 7.32 (t, *J* = 7.3 Hz, 4H), 7.24 (t, *J* = 7.3 Hz, 4H). FAB-MS: *m*/*z* 603[M + H]<sup>+</sup>.

2,2'-Dimethyl-[1,1'-biphenyl]-4,4'-diamine (26). 3-Methylnitrobenzene (5.0 g, 36.5 mmol) and zinc powder (13.8 mg, 21.1 mmol) were added to ethanol under a N<sub>2</sub> atmosphere and the mixture was refluxed. 30% aqueous NaOH (25 mL) was added dropwise to the mixture and refluxed for 4 h. After the filtration of the resultant mixture, the filtrate was added to the mixture of acetic acid (22.5 mL) and 0.5 M aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (50 mL). The precipitate was filtered off and the filtrate was extracted with Et<sub>2</sub>O. The organic phase was washed with saturated aqueous NaHCO<sub>3</sub> and brine and dried with Na<sub>2</sub>SO<sub>4</sub>. After evaporation of solvent, a mixture of 1,2-bis(3-methylphenyl) hydrazine (25) (72%) and 3-methylnitrobenzene was obtained. This mixture was used in the next step without further purification.

To the degassed aqueous HCl under reflux, the mixture of 1,2-bis(3-methylphenyl)hydrazine (72%) and 3-methylnitrobenzene (1.0 g) was added and refluxed for 5 h under a N<sub>2</sub> atmosphere. After filtration of the resultant mixture, the filtrate was heated with activated charcoal for 30 min. After removal of the activated charcoal, 20% aqueous NaOH was added to the solution. The mixture was extracted with Et<sub>2</sub>O, and the organic phase was washed with water and brine and dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure to give **26** as a brown oil (691 mg, 31%). This was used in the next step without further purification.

**4,4'-Dibromo-2,2'-dimethyl-1,1'-biphenyl (27).** 2,2'-Dimethyl-[1,1'-biphenyl]-4,4'-diamine (691 mg, 3.26 mmol) was dissolved in 10% aqueous H<sub>2</sub>SO<sub>4</sub> (7.0 mL) at 10 °C and NaNO<sub>2</sub> (492 mg, 7.16 mmol) in H<sub>2</sub>O (4.0 mL) was added dropwise to the solution at 10 °C. After stirring for 30 minutes, CuBr (4.67 g, 32.6 mmol) in 48% aqueous HBr (45.0 mL) was added to the reaction mixture and the mixture was stirred at 50 °C for 3 h. After cooling to room temperature, the solution was extracted with Et<sub>2</sub>O. The organic phase was washed with 3 M aqueous HCl and water and dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced pressure. The product was purified by silica gel column chromatography (hexane) to give **27** as a transparent oil (393 mg, yield: 55%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.40 (s, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 6.90 (d, *J* = 7.8 Hz, 2H), 1.98 (s, 6H).

2,2'-Dimethyl-[1,1'-biphenyl]-4,4'-dicarbaldehyde (28). Compound 27 (256 mg, 0.75 mmol) was dissolved in dry THF (3.0 mL) and cooled to -78 °C. 1.55 M *n*-BuLi in hexane (1.16 mL) was added dropwise and the solution was stirred for 30 min at -78 °C. Dry DMF (0.14 mL) and dry THF (1 mL) were added dropwise and the reaction mixture was warmed to room temperature and stirred for 3 h. The reaction was quenched with 3 M aqueous HCl and the solution was extracted with Et<sub>2</sub>O. The organic phase was washed with saturated aqueous NaHCO<sub>3</sub>, water and brine and dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced pressure. The product was purified by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>: hexane = 2 : 1) to give **28** as a transparent oil (118 mg, yield: 66%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  10.01 (s, 2H), 7.99 (s, 2H), 7.94 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 2.10 (s, 6H).

4,4'-Bis(4,5-diphenyl-1*H*-imidazol-2-yl)-2,2'-dimethyl-1,1'biphenyl (29). Compound 28 (40 mg, 0.17 mmol), benzil (88 mg, 0.42 mmol) and ammonium acetate (259 mg, 3.36 mmol) in acetic acid (4.0 mL) were stirred at 110 °C overnight. The reaction mixture was allowed to cool to room temperature, neutralized by aqueous ammonia and filtered. The mixture was washed with water and ethanol to give 29 as a white powder (68 mg, yield: 65%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  12.69 (s, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 7.3 Hz, 4H), 7.45 (t, *J* = 7.3 Hz, 4H), 7.38 (t, *J* = 7.3 Hz, 4H), 7.24 (t, *J* = 7.3 Hz, 4H), 2.13 (s, 6H). FAB-MS: *m*/z 618[M + H]<sup>+</sup>.

1,2'-Bis(3,5'-dimethylphenyl)hydrazine (30). 3,5'-Dimethylnitrobenzene (9.98 g, 66.0 mmol) and zinc powder (25.0 g, 15.3 mmol) were added to ethanol (40 mL) under a N<sub>2</sub> atmosphere and the mixture was refluxed. 30% aqueous NaOH (50 mL) was added dropwise to the mixture and refluxed for 4 h. After the filtration of the resultant mixture, the filtrate was added to the mixture of 30% acetic acid aq. and 0.5 M aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> (150 mL). The precipitate was filtered and extracted with hot methanol. The extract was added to acetic acid and cooled to 10 °C. The precipitate was filtered and extracted with Et<sub>2</sub>O. The organic phase was washed with saturated aqueous NaHCO<sub>3</sub> and brine and dried *in vacuo* to give the desired product (5.52 g, 35%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ 6.64 (s, 6H), 5.42 (s, 2H), 2.20 (s, 12H).

2,2',6,6'-Tetramethyl-[1,1'-biphenyl]-4,4'-diamine (31). To degassed aqueous HCl (260 mL) under reflux, compound 30 (5.52 g, 15.06 mmol) was added and refluxed for 5 h under a N<sub>2</sub> atmosphere. After filtration of the resultant mixture, the filtrate was heated with activated charcoal for 30 min. After the removal of the activated charcoal, 20% aqueous NaOH was added to the solution. The aqueous solution of saturated aqueous AcONa was added to the solution and the mixture was extracted with Et<sub>2</sub>O. The organic phase was dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was washed with hot benzene/hexane to give compound 31 (3.55 g, 64%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  6.67 (s, 6H), 3.58 (s, 4H), 1.79 (s, 12H).

4,4'-Dibromo-2,2',6,6'-tetramethyl-1,1'-biphenyl (32). 2,2',6,6'-Tetramethyl-[1,1'-biphenyl]-4,4'-diamine (3.42 g, 14.2 mmol) was dissolved in 10% aqueous  $H_2SO_4$  (31.4 mL) at 10 °C and NaNO<sub>2</sub> (2.14 g, 31.1 mmol) in  $H_2O$  (20 mL) was added dropwise to the solution at 10 °C. After stirring for 30 minutes, CuBr (21.4 g, 149 mmol) in 48% aqueous HBr (214 mL) was added to the reaction mixture and the mixture was stirred at 50 °C for 3 h. After cooling to room temperature, the solution was extracted with Et<sub>2</sub>O. The organic phase was washed with 3 M aqueous HCl and water and dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced pressure. The product was purified by alumina gel column chromatography (Et<sub>2</sub>O) to give **32** (2.23 g, yield: 43%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.28 (s, 4H), 1.82 (s, 12H).

2,2',6,6'-Tetramethyl-[1,1'-biphenyl]-4,4'-dicarbaldehyde (33). Compound 32 (2.12 g, 5.98 mmol) was dissolved in dry THF 3.0 mL and cooled to -78 °C. 1.55 M *n*-BuLi in hexane (8.17 mL) was added dropwise and the solution was stirred for 30 min at -78 °C. The mixture of dry DMF (1.38 mL) and dry THF (50 mL) was added dropwise and the reaction mixture was warmed to room temperature and stirred for 3 h. The reaction was quenched with 3 M aqueous HCl and the solution was extracted with Et<sub>2</sub>O. The organic phase was washed with saturated aqueous NaHCO<sub>3</sub>, water and brine and dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced pressure. The product was purified by silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub> : hexane = 2 : 1) to give **33** as a transparent oil (437 mg, yield: 28%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  9.96 (s, 2H), 7.64 (s, 4H), 1.93 (s, 12H).

**4,4'-Bis(4,5-diphenyl-1***H***-imidazol-2-yl)-2,2',6,6'-tetramethyl-1,1'-biphenyl (34).** Compound 33 (40 mg, 0.17 mmol), benzil (88 mg, 0.42 mmol) and ammonium acetate (259 mg, 3.36 mmol) in acetic acid (4.0 mL) were stirred at 110 °C overnight. The reaction mixture was allowed to cool to room temperature, neutralized by aqueous ammonia and filtered. The mixture was washed with water and ethanol to give 34 as a white powder (71 mg, yield: 64%). <sup>1</sup>H NMR (500 MHz, DMSO $d_6$ ):  $\delta$  12.65 (s, 2H), 7.92 (d, *J* = 8.0 Hz, 4H), 7.56 (t, *J* = 6.7 Hz, 4H), 7.51 (t, *J* = 6.7 Hz, 4H), 7.45 (t, *J* = 6.5 Hz, 4H), 7.37 (t, *J* =



Scheme 7 Synthesis of R1.



Scheme 8 Synthesis of R2.



Scheme 9 Synthesis of R3.

6.5 Hz, 2H), 7.31 (t, J = 6.5 Hz, 4H), 7.29 (t, J = 6.5 Hz, 2H), 1.96 (s, 12H). FAB-MS: m/z 646[M + H]<sup>+</sup>.

General procedure for the syntheses of R1, R2 and R3. To a solution of the precursor lophine derivative (0.04 mmol) in 40 mL degassed benzene was added 15% aqueous KOH (10 mL). A solution of potassium ferricyanide (1.0 g, 3.30 mmol) was added to the solution and dried with Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure to give a photochromic solid. This was used for absorption spectroscopy after UV light irradiation in benzene (Schemes 7–9).

#### Conflicts of interest

There are no conflicts to declare.

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