



Distyryl 1,2-Bis(2-pyridylmethoxy) benzene substituted near-infrared BODIPY photosensitizers: synthesis and spectroscopic studies

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Abstract. Near-infrared BODIPY photosensitizers with symmetrical 2,6-diiodo 3,5-distyryl 1,2-Bis(2-pyridylmethoxy) benzene were synthesized to study the singlet oxygen ($^1\text{O}_2$) photosensitizing efficiency as triplet photosensitizer as well as fluorescent sensors for metal cation recognition. Moderate singlet oxygen ($^1\text{O}_2$) quantum yield (Φ_Δ) was obtained for the photosensitizers. Emission intensity of the photosensitizers increased *ca.* by 1.4-2-fold upon addition of Hg^{2+} and Fe^{2+} ions. The discussed results are useful to design near-infrared photosensitizers with long lived triplet excited states for various applications such as PDT, fluorescent bioimaging and sensor materials.

Keywords. BODIPY; near-infrared (NIR); singlet oxygen ($^1\text{O}_2$); 1,2-bis(2-pyridylmethoxy) benzene; metal cations; photodynamic therapy (PDT); distyryl.

1. Introduction

In the past decades, near-infrared (NIR) fluorescent dyes based on 4,4-Difluoro-4-bora 3a,4a-diaza-s-indacene (BODIPY) have drawn enormous attention as fluorescent probes and bioimaging materials.¹⁻⁸ In addition, BODIPY, like Phthalocyanines have been explored as photosensitizers for photodynamic therapy (PDT)⁹ owing to its strong tendency to absorb at visible region with strong absorbance, to emit narrow emission peaks with high quantum yield, quite insensitive to the polarity and pH of the respective surrounding making them comparatively stable to physiological conditions and to permit the tuning of photophysical properties on slight structural modifications. Moreover, due to cellular imaging in the NIR region has deep tissue perforation, negligible

photodamage to tissues and less bioauto-fluorescence,¹⁰⁻¹³ BODIPY photosensitizers exhibiting absorption and emission in the NIR region (650 nm–900 nm) are more ideal for PDT.

An ideal photosensitizer which is the key component of PDT should exhibit strong absorption at NIR wavelengths (650–900 nm) for deep tissue penetration, generate high singlet oxygen ($^1\text{O}_2$) quantum yield (Φ_Δ) with negligible dark toxicity and enhance the selective immune response against diseased tissues without affecting the healthy tissues.¹⁴ Most commonly used porphyrin-based photosensitizers for PDT exhibit weak absorption in the visible region and induce side effects on photoirradiation, damaging the normal tissues. Thus, designing and developing photosensitizers with strong absorption in the NIR region and strong fluorescence along with long-lived triplet excited states i.e. satisfactory intersystem crossing (ISC) to

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sensitize singlet oxygen ($^1\text{O}_2$) has become a challenge.^{14,15} Photosensitizers exhibiting long-lived triplet excited state as well as strong fluorescence can be used for various applications such as PDT, fluorescent bioimaging and sensors materials.¹⁶⁻²¹

Concerning these aspects, we have prepared two BODIPY photosensitizers **BDPY-DBPMB** and **NBDPY-DBPMB** with 1,2-bis(2-pyridylmethoxy) benzene distyryl moiety at 3,5-positions of the BODIPY core to approach the absorption/emission in the NIR wavelength. Further, 2,6-iodination of **BODIPY** core increases the rate of singlet to triplet state inter system crossing (ISC).²²⁻²⁵ As a result, generation of singlet oxygen ($^1\text{O}_2$) quantum yield (Φ_Δ) with long-lived triplet excited states is increased due to heavy atom effect of iodine. The photophysical properties have been measured with a steady state and time-resolved spectroscopy. **BDPY-DBPMB** and **NBDPY-DBPMB** were used as triplet photosensitizers for generation of singlet oxygen ($^1\text{O}_2$). BODIPY fluorophore **BDPY-DBPMB** and **NBDPY-DBPMB** bearing 2,6-distyryl 1,2-bis(2-pyridylmethoxy) benzene, used as ligand for detection of various metal cations, exhibits increased fluorescence with Hg^{2+} and Fe^{2+} ions, respectively.

2. Experimental

2.1 Materials and Physical measurements

All the synthetic precursors were commercially available and used as received. Solvents were dried and distilled prior to synthesis. ^1H and ^{13}C NMR spectra were recorded on a Bruker-Avance 400 and 100 MHz spectrometer, respectively (CDCl_3 as solvent, TMS as standard, $\delta = 0.00$ ppm). Fluorescence spectra were measured on a Fluorolog-3 (Spex model, Jobin Yvon) spectrofluorometer. Electronic absorption spectra were recorded on a Shimadzu (Model UV-3600) spectrophotometer. Absorption spectra were recorded on a Shimadzu UV-3600, UV/VIS spectrophotometer. High resolution mass spectra (HRMS) were determined on a MALDI TOF Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron-HiRes, Power: 85 spectrometer. The transient absorption spectra were recorded on a LKS-20 laser nanosecond flash photolysis kinetic spectrometer using OCR-12 Series Quanta Ray Nd:YAG laser. The laser energy was 110 mJ at 355 nm. 200 W xenon lamp (model 3767) on an Oriel optical bench (model 11200) with a grating monochromator, was used as a light source to carry out the Photo-bleaching experiments. Oriel photodiode detection system (model 7072) was used to maintain constant intensity throughout the irradiation.

2.2 Synthesis of Bodipy dyes 1 and 2

Bodipy dyes (**1a**),²⁶ (**1b**),²⁷ (**2a**),²⁶ (**2b**)²⁷ and compound (**3**)²⁸ were synthesized following the literature methods.

2.3 Synthesis of compound BDPY-DBPMB

To a solution of **2a** (0.200 mmol, 115 mg) and compound **3** (0.400 mmol, 128 mg) in dry benzene (20 mL), acetic acid (0.6 mL) and piperidine (1.0 mL) were added. The reaction mixture was heated at 80 °C under reflux with a Dean Stark trap to remove the water generated by the condensation. The reaction was monitored by TLC ($\text{CHCl}_3/\text{MeOH} = 95/5$, v/v as eluent). After consumption of all the starting materials, the reaction mixture was cooled to room temperature. The solvent was evaporated under reduced pressure, and the crude product thus obtained was purified by column chromatography (silica gel, $\text{CHCl}_3/\text{MeOH} = 95/5$, v/v as eluent). The green solid was obtained as compound **BDPY-DBPMB**. Yield: 44% (104 mg). MALDI-HRMS: calcd ($[\text{C}_{57}\text{H}_{45}\text{BF}_2\text{I}_2\text{N}_6\text{O}_4]^+$), $m/z = 1180.16$, found, $m/z = 1180.84$. ^1H NMR (δ , ppm in CDCl_3 , 400 MHz): 8.61–8.58 (m, 4H), 8.02 (d, 2H, $J = 16$ Hz), 7.72–7.66 (m, 6H), 7.62 (d, 2H, $J = 8$ Hz), 7.58 (d, 2H, $J = 8$ Hz), 7.53–7.47 (m, 5H), 7.23–7.21 (m, 6H), 7.16–7.13 (m, 2H), 6.94 (d, 2H, $J = 8$ Hz), 5.37 (s, 4H), 5.35 (s, 4H), 1.43 (s, 6H). ^{13}C NMR (δ , ppm in CDCl_3 , 100 MHz): δ 157.17, 150.46, 149.64, 149.20, 148.53, 145.74, 139.14, 138.67, 136.82, 135.28, 132.98, 130.64, 129.45, 128.34, 122.67, 122.05, 121.44, 121.24, 117.45, 114.20, 113.60, 83.29, 71.97, 71.59, 17.52.

2.4 Synthesis of compound NBDPY-DBPMB

To a solution of **2b** (0.200 mmol, 124 mg) and compound **3** (0.400 mmol, 128 mg) in dry benzene (20 mL), acetic acid (0.6 mL) and piperidine (1.0 mL) were added. Thereafter the synthetic procedure is similar to that of compound **BDPY-DBPMB**; a dark green solid was obtained as compound **NBDPY-DBPMB**. Yield: 41% (100 mg). MALDI-HRMS: calcd ($[\text{C}_{57}\text{H}_{44}\text{BF}_2\text{I}_2\text{N}_7\text{O}_6 + \text{H}]^+$), $m/z = 1226.16$, found, $m/z = 1226.36$; calcd ($[\text{C}_{57}\text{H}_{44}\text{BF}_2\text{I}_2\text{N}_7\text{O}_6]^+$), $m/z = 1225.15$, found, $m/z = 1225.15$. ^1H NMR (δ , ppm in CDCl_3 , 400 MHz): 8.61–8.58 (m, 4H), 8.42 (d, 2H, $J = 8$ Hz), 8.07 (d, 2H, $J = 16$ Hz), 7.73–7.66 (m, 4H), 7.62 (d, 2H, $J = 8$ Hz), 7.59–7.54 (m, 4H), 7.51–7.47 (m, 2H), 7.28–7.27 (m, 2H), 7.25–7.21 (m, 4H), 7.17–7.14 (m, 2H), 6.96–6.94 (m, 2H), 5.37 (s, 4H), 5.35 (s, 4H), 1.42 (s, 6H). ^{13}C NMR (δ , ppm in CDCl_3 , 100 MHz): δ 157.18, 150.48, 149.65, 149.29, 148.53,

145.74, 139.99, 139.15, 136.83, 135.29, 132.98, 130.65, 129.45, 128.35, 124.58, 122.68, 122.05, 121.44, 121.24, 117.45, 114.21, 113.62, 83.28, 71.97, 71.58, 17.52.

2.5 Singlet oxygen (1O_2) quantum yields (Φ_Δ) by DPBF assay

Singlet oxygen (1O_2) quantum yields (Φ_Δ) of the photosensitizers **BDPY-DBPMB** and **NBDPY-DBPMB** were measured using Methylene Blue (MB) ($\Phi_\Delta = 0.49$ in DMSO) as standard.²⁹⁻³¹ Quantum yields for singlet oxygen generation in DMSO (200 μ l) were determined by monitoring the photooxidation of 1,3-diphenylisobenzofuran (DPBF) (2 μ l, 8×10^{-3} M) sensitized by different concentrations of the photosensitizers **BDPY-DBPMB** and **NBDPY-DBPMB** in DMSO. DPBF was used as the 1O_2 trapping agent. The photosensitizers were irradiated with 640–720 nm wavelength using Waldmann PDT-1200 Lamp (Waldmann, Villingen-Schwenningen, Germany) at a light dose of 20 J/cm². Absorbance at 410 nm at regular intervals was recorded in a microplate reader (Multiskan Spectrum Elisa Reader, Thermo Fisher Scientific) to estimate the quenched absorbance of DPBF. The slope of the curves of absorbance maxima of DPBF at 410 nm versus irradiation time for each photosensitizer were calculated. Singlet oxygen quantum yield (Φ_Δ) were calculated according to the equation (eqn (1)):

$$\Phi_{\Delta\text{sam}} = \Phi_{\Delta\text{std}} \left(\frac{m_{\text{sam}}}{m_{\text{std}}} \right) \left(\frac{F_{\text{std}}}{F_{\text{sam}}} \right) \quad (1)$$

where “sam” and “std” designate the “photosensitizers **BDPY-DBPMB** and **NBDPY-DBPMB**” and “MB”, respectively. “m” is the slope of difference in change in absorbance of DPBF (at 425 nm) with the irradiation time, “F” is the absorption correction factor, which is given by $F = 1 - 10^{-\text{OD}}$ (OD is the absorbance at the irradiation wavelength).

2.6 Metal Ion Sensing

Stock solutions (20 $\times 10^{-3}$ M) of all the metal salts (CaCl₂, NaCl, ZnCl₂, LiCl, CdCl₂, HgCl₂, CsBr, CuCl₂, PdCl₂, FeBr₂, MgBr₂, NiCl₂ and KCl) were prepared in DMSO/distilled water (90:10). Stock solutions of photosensitizers (1 $\times 10^{-3}$ M) **BDPY-DBPMB** and **NBDPY-DBPMB** were prepared in

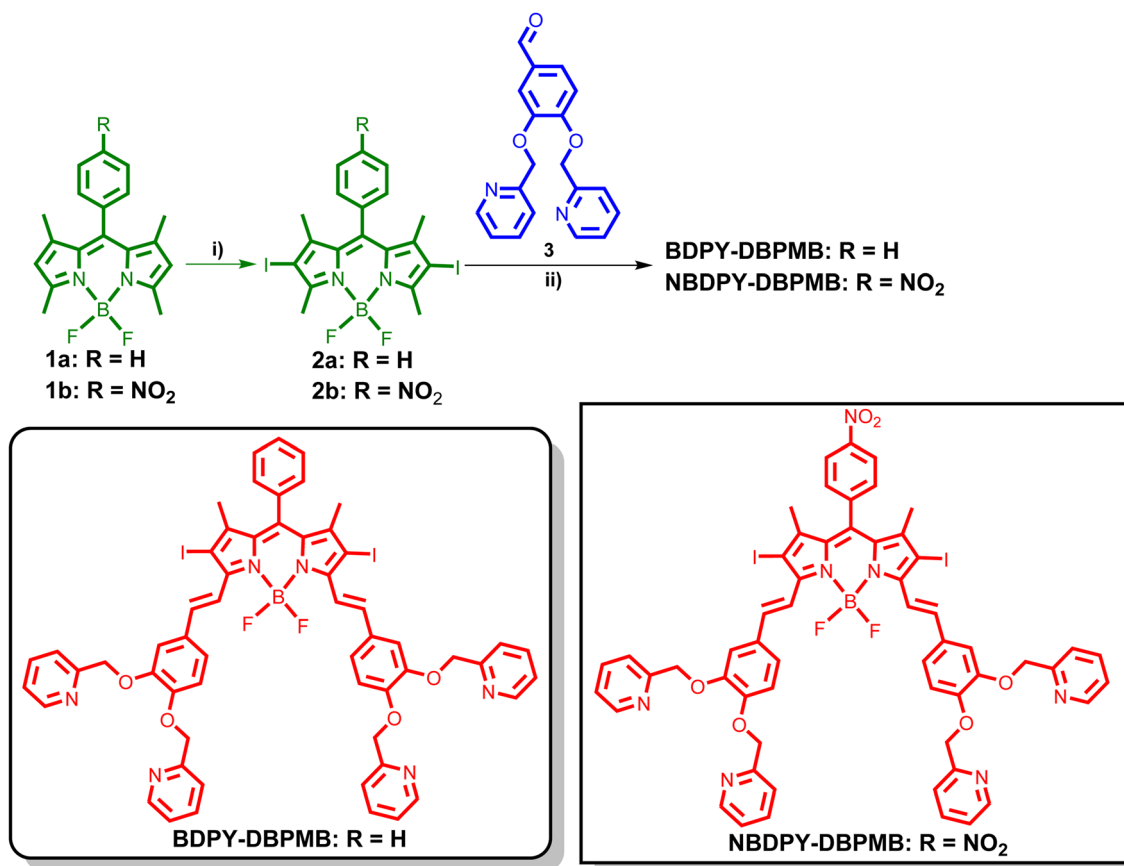
DMSO. The solution was allowed to stand for 2 min before taking each spectral measurement.

3. Results and Discussions

Our approach to prepare 2,6-diiodo 3,5-symmetric distyryl BODIPY photosensitizers **BDPY-DBPMB** and **NBDPY-DBPMB** has been rationalized on the fact to extend the absorption/emission in the NIR wavelength as well as to access efficient singlet-to-triplet intersystem crossing (ISC) by heavy atom effect Scheme 1.

First, we attached the iodine atom to the BODIPY fluorophore core **1** to accelerate the ISC. The 2-fold Knoevenagel condensation reaction of 2,6-diiodo BODIPY **2** with 3,4-bis(2-pyridylmethoxy) benzaldehyde **3** led to the formation of 3,5-distyryl BODIPY photosensitizers **BDPY-DBPMB** (yield = 44%) and **NBDPY-DBPMB** (yield = 41%). The molecular structure of **BDPY-DBPMB** and **NBDPY-DBPMB** were confirmed by ¹H NMR, ¹³C NMR and MALDI-HRMS. The data were reliable with the previously reported distyryl BODIPY derivatives.³² The characterization spectra are given in the Supplementary Information.

The UV-Vis absorption Figure 1a and emission Figure 1b spectra of the diiodo styryl BODIPY **BDPY-DBPMB** and **NBDPY-DBPMB** were studied in DMSO. **BDPY-DBPMB** and **NBDPY-DBPMB** displayed absorption in the NIR region due to the large extended π -conjugation at 671 nm ($\epsilon = 9.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) and 682 nm ($\epsilon = 1.22 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), respectively. The emission spectra were observed at 708 nm and 724 nm for **BDPY-DBPMB** and **NBDPY-DBPMB**, respectively Table 1. Electron-donating bis(pyridin-2-ylmethoxy) group (push) at 3,5-positions and electron-withdrawing nitro group (pull) at the para position of 8-phenyl in the electron deficient BODIPY core (pull) originates a strong electron push-pull effect in the **NBDPY-DBPMB** dye (Scheme 2). Thus, the red shift (ca.16 nm) for nitro substituent in **NBDPY-DBPMB** is attributed to the presence of strong electron push-pull substituents to a BODIPY fluorophore (Scheme 2) through the formation of intramolecular charge-transfer (ICT) state in polar solvent.³³⁻³⁵ **BDPY-DBPMB** and **NBDPY-DBPMB** exhibit Stokes shifts at 37 nm and 42 nm, respectively. Though **NBDPY-DBPMB** shows red-shift emission, large Stokes shift was not observed as compare to **NBDPY-DBPMB**.



Scheme 1. Synthesis of the BODIPY dyes **BDPY-DBPMB** and **NBDPY-DBPMB**. Reagents and conditions: i) NIS (2 eq.), dry DCM, r.t., 4 h.; (ii) 3,4-bis(pyridin-2-ylmethoxy) benzaldehyde **3** (2 eq.), dry benzene, piperidine, AcOH, 80 °C, reflux.

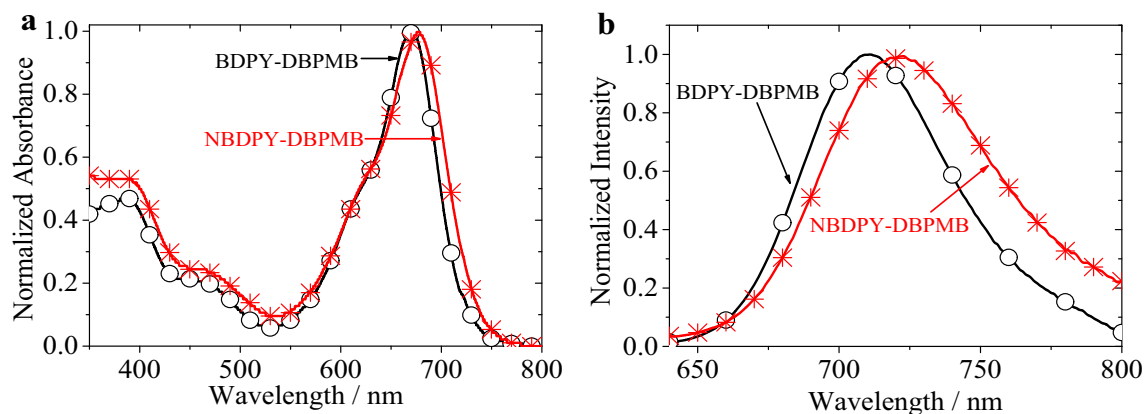


Figure 1. (a) Normalized UV-Vis absorption spectra of **BDPY-DBPMB** and **NBDPY-DBPMB** and (b) normalized fluorescence spectra of **BDPY-DBPMB** and **NBDPY-DBPMB**. ($\lambda_{\text{ex}} = 630 \text{ nm}$, $c = 1.0 \times 10^{-5} \text{ M}$ in DMSO).

The nanosecond time-resolved transient difference absorption spectra studies were carried out to investigate the triplet excited states of the reported diiodo photosensitizers Figure 2 and Figure S7, Supplementary Information in DMSO. Upon 355 nm pulsed laser excitation, positive transient absorption (TA) bands at 440 nm, 540 nm and 770 nm were observed due to the

absorption of triplet excited state of **BDPY-DBPMB** Figure 2a. In addition, bleaching band at 671 nm alike the UV-Vis absorption spectra Figure 1a arises due to the depletion of ground state of **BDPY-DBPMB** photosensitizer. The lifetime of the **BDPY-DBPMB** and **NBDPY-DBPMB** transients, were found to be 0.65 μs and 1.44 μs , respectively Figure 2b and

Table 1. Photophysical Properties of **BDPY-DBPMB** and **NBDPY-DBPMB** in DMSO

Photosensitizers	$\lambda_{\text{abs}}^{\text{a}}/\text{nm}$	ϵ^{b}	$\lambda_{\text{em}}^{\text{a}}/\text{nm}$	Φ_{Δ}^{c}	$\tau_{\text{T}}^{\text{d}} [\mu\text{s}]$
BDPY-DBPMB	671	0.094	708	0.51	0.65
NBDPY-DBPMB	682	0.122	724	0.41	1.44

^a $c = 1.0 \times 10^{-5}$ M in DMSO. ^b Molar extinction coefficient at the absorption maxima. ϵ : $10^5 \text{M}^{-1}\text{cm}^{-1}$. ^c Singlet oxygen ($^1\text{O}_2$) generation quantum yield measured using methylene blue ($\Phi_{\Delta} = 0.49$ in DMSO) as a reference ^d Triplet excited state lifetimes, measured by nanosecond time-resolved transient absorptions.

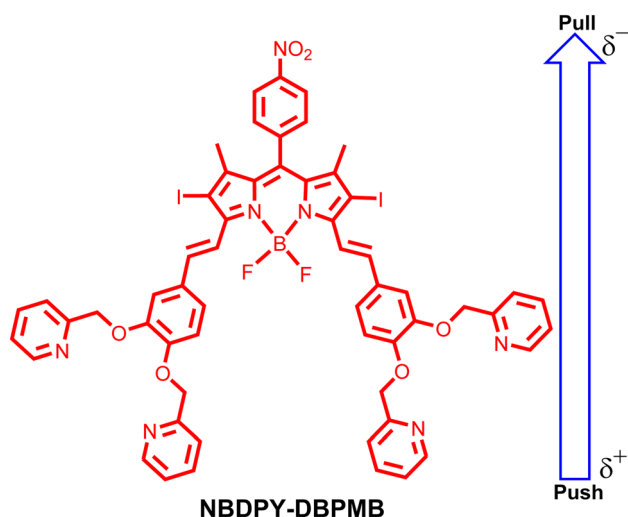
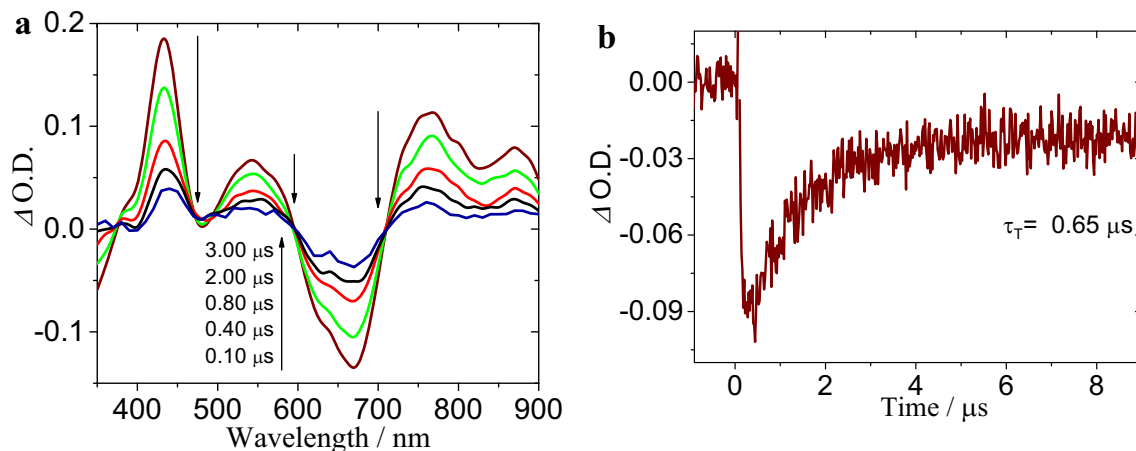
**Scheme 2.** Dipolar “Push–Pull” chromophores surrounding BODIPY core.

Figure S7, Supplementary information. Since, the decay lifetime of transient positive band is in μs , the presence of the singlet excited state is excluded. The fluorescence lifetime for singlet excited state should be <1 ns.^{25,36}

The photostability of **BDPY-DBPMB** and **NBDPY-DBPMB** photosensitizers were determined on continuous irradiation with 200 W xenon lamp for 2 h.

The pre- and post-irradiation exhibited identical absorbance spectra indicating high photostability of the photosensitizers Figure 3.

Due to the presence of heavy iodine atom, the photosensitizers **BDPY-DBPMB** and **NBDPY-DBPMB**, exhibiting triplet excited lifetime of 0.65 μs and 1.44 μs , respectively are explored for the singlet oxygen ($^1\text{O}_2$) generation. Thus, $^1\text{O}_2$ photosensitizing ability of **BDPY-DBPMB** and **NBDPY-DBPMB** as triplet photosensitizers were studied *via* the bleaching of 1,3-diphenylisobenzofuran (DPBF) as the $^1\text{O}_2$ scavenger in DMSO and methylene blue as standard Figure 4 and Table 1. Singlet oxygen ($^1\text{O}_2$) quantum yield (Φ_{Δ}) values of the photosensitizers **BDPY-DBPMB** and **NBDPY-DBPMB** were 51% and 41%, respectively. Since, the absorption of **BDPY-DBPMB** in the visible region is slightly stronger than **NBDPY-DBPMB**, the $^1\text{O}_2$ photosensitizing ability of **BDPY-DBPMB** is somewhat more efficient than **NBDPY-DBPMB**.

**Figure 2.** (a) Nanosecond Transient absorption spectra of **BDPY-DBPMB** and (b) decay traces of **BDPY-DBPMB** after pulsed excitation at 355 nm laser. $c = 1.0 \times 10^{-6}$ M in DMSO.

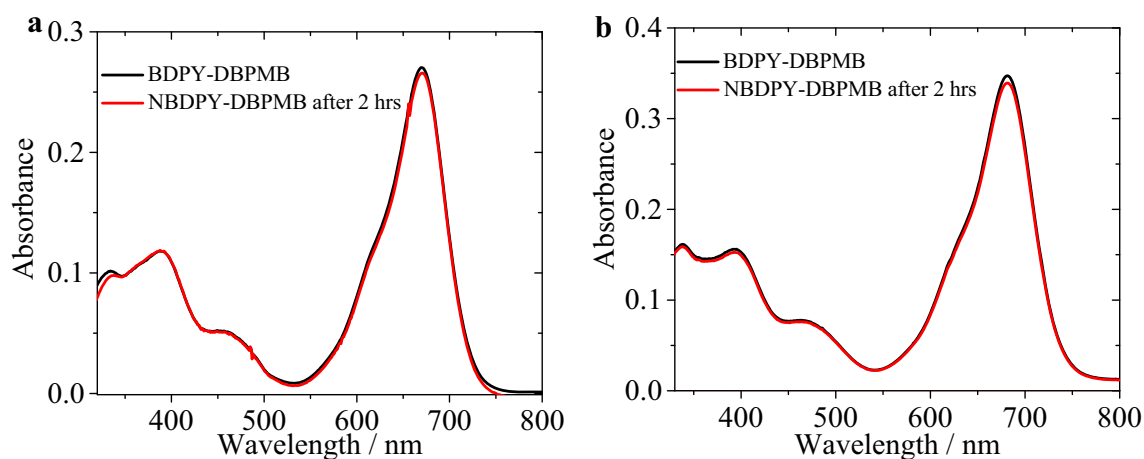


Figure 3. Absorption spectra of (a) **BDPY-DBPMB** and (b) **NBDPY-DBPMB**, upon two hours irradiation with oriel lamp (200W xenon lamp, model 3767) on an Oriel optical bench (model 11200).

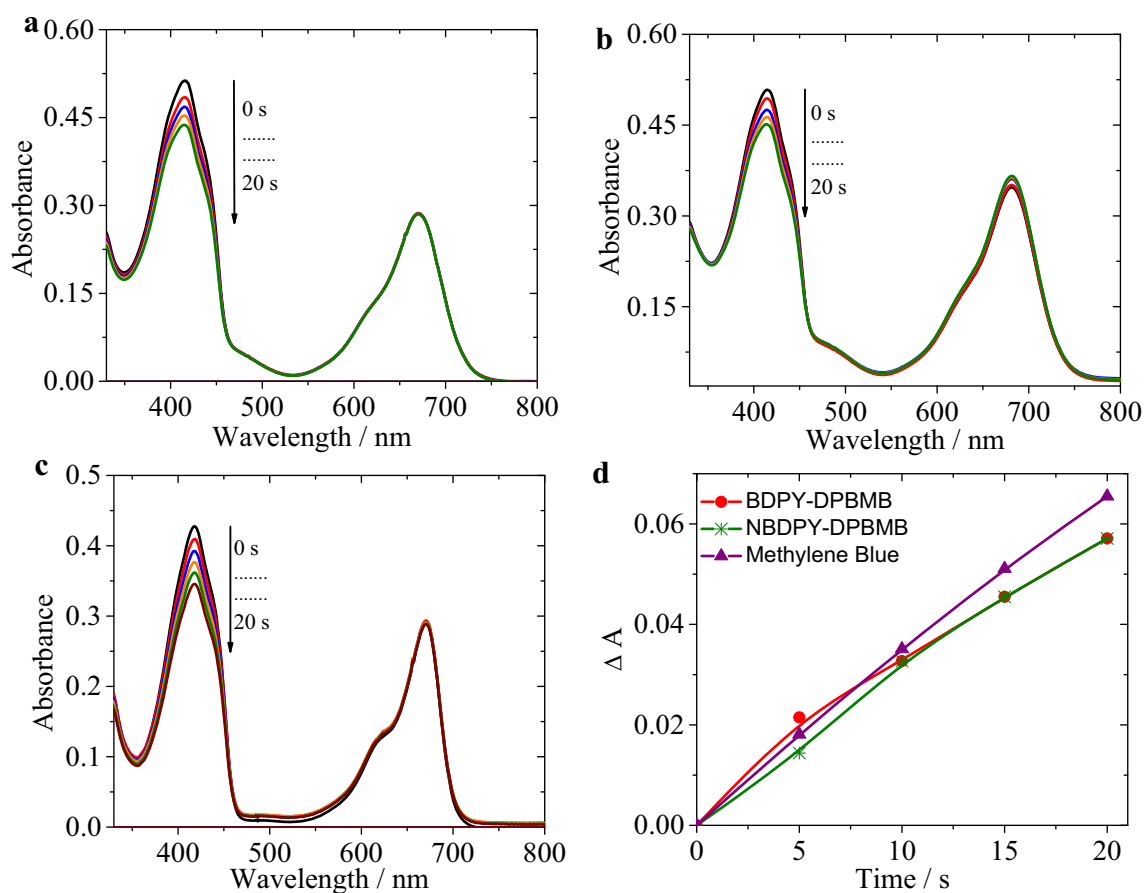


Figure 4. Decrease in UV-Vis absorption of DPBF at $\lambda_{\text{abs}} = 410 \text{ nm}$ using photosensitizers: (a) **BDPY-DBPMB**; (b) **NBDPY-DBPMB**; (c) **Methylene Blue** as the standard.; (d) Plots of ΔA of DPBF vs Irradiation time with photosensitizers **BDPY-DBPMB**, **NBDPY-DBPMB** and **Methylene Blue**.

Singlet oxygen ($^1\text{O}_2$) photosensitizing ability of the triplet photosensitizers can be switched ON or OFF by changing the pH of solution. This technique has been used to design targeting PDT reagents to selectively get activated by the acidic microenvironment of the tumour tissue.^{14,37,38} Thus, the effect of addition of

trifluoroacetic acid (TFA) to photosensitizers **BDPY-DBPMB** and **NBDPY-DBPMB** solution in DMSO was investigated. No visible colour change and shift in absorption spectra Figure S8a and Figure S8c, Supplementary Information was observed on protonation of pyridyl moiety of photosensitizers **BDPY-DBPMB**

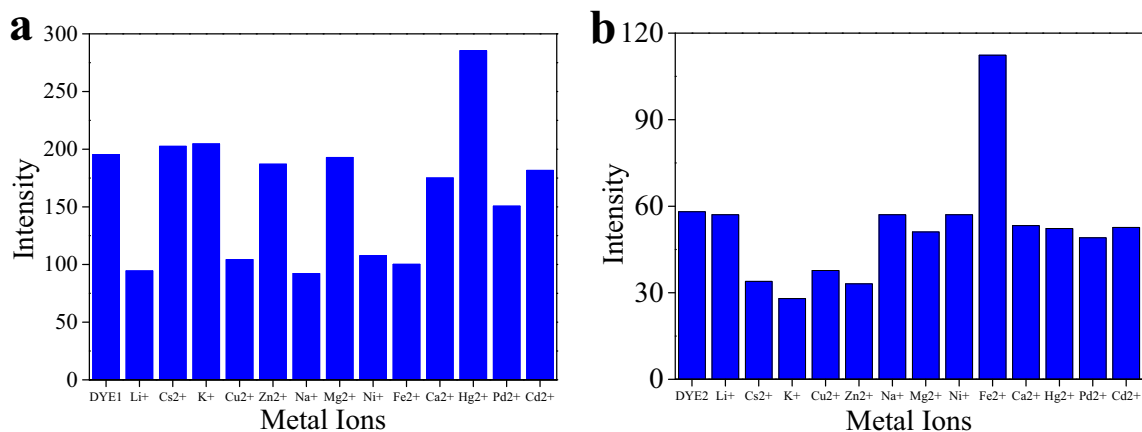


Figure 5. Histogram of (a) **BDPY-DBPMB** (DYE1) and (b) **NBDPY-DBPMB** (DYE2), based on emission intensities at 724 nm in DMSO/distilled water (90:10) upon addition of various metal ions (80 eq.). $\lambda_{\text{ex}} = 630 \text{ nm}$, $c = 5.0 \times 10^{-6} \text{ M}$ in DMSO.

and **NBDPY-DBPMB**. Only minute change in emission intensity of **BDPY-DBPMB** and **NBDPY-DBPMB** was observed after protonation by TFA Figure S9b and S9d, Supplementary Information, possibly either due to the electron accepting character of the BODIPY or the interactive effects of the protonated nitrogen of pyridyl moiety induces push-pull effect in BODIPY core, changing the intermolecular packing and molecular conformation upon acid protonation.¹⁷ Negligible change in singlet oxygen ($^1\text{O}_2$) quantum yield (Φ_{Δ}) of the photosensitizers **BDPY-DBPMB** and **NBDPY-DBPMB** was found (Table S1, Supplementary Information).

To study the sensitivity of ligand 1,2-bis(2-pyridylmethoxy) benzene in **BDPY-DBPMB** and **NBDPY-DBPMB** as sensors, absorption/emission spectra of the **BDPY-DBPMB** and **NBDPY-DBPMB** upon addition of several 80 equivalent of metal cations Ca^{2+} , Na^+ , Zn^{2+} , Li^+ , Cd^{2+} , Hg^{2+} , Cs^+ , Cu^{2+} , Pd^{2+} , Fe^{2+} , Mg^{2+} , Ni^{2+} and K^+ were measured in DMSO/distilled water (90:10). Absorption/emission spectra exhibited no pertinent bathochromic or hypsochromic shift Figures S10 and S11, Supplementary Information. No significant changes were observed in the absorption spectroscopy of **BDPY-DBPMB** and **NBDPY-DBPMB** Figure S10, Supplementary Information. However, the emission intensity of **BDPY-DBPMB** and **NBDPY-DBPMB** increased 1.5-fold and 2-fold upon the addition of 80 equivalents of Hg^{2+} and Fe^{2+} , respectively Figure 5 and Figure S11, Supplementary Information whereas the other cations could not induce any significant enhancement in the emission spectra. The probable binding mechanism is depicted in Figure 6. On photoirradiation of **BDPY-DBPMB**, emission of the BODIPY moieties quenched by a

photoinduced electron transfer (PET) mechanism between the electron donating ligand 1,2-bis(2-pyridylmethoxy) benzene and BODIPY fluorophore. On addition of Hg^{2+} , the PET process is switched off through the complexation of the 1,2-bis(2-pyridylmethoxy) benzene PET donor enhancing the emission intensity. On the other hand, emission intensity is decreased for **BDPY-DBPMB** in the presence of Cu^{2+} and Pd^{2+} , and for **NBDPY-DBPMB** in the presence of K^+ , Cu^{2+} and Zn^{2+} . The exact reason for this discrepancy for ion selectivity by **BDPY-DBPMB** and **NBDPY-DBPMB** is still not clear. These results imply that photosensitizers **BDPY-DBPMB** and **NBDPY-DBPMB** could be utilized as fluorescent sensors for the selective detection of Hg^{2+} and Fe^{2+} .

4. Conclusions

In conclusion, we prepared two symmetrical diiodo 1,2-bis(2-pyridylmethoxy) benzene-distyryl photosensitizers, **BDPY-DBPMB** and **NBDPY-DBPMB** in good yields which show both NIR absorption/emission and short-lived triplet excited states. The BODIPY dyes were used as triplet photosensitizers to study the $^1\text{O}_2$ photosensitizing efficacy as well as fluorescent sensors for metal cation recognition. In presence of cations Hg^{2+} and Fe^{2+} , ca.1.5-fold and 2-fold emission intensity was increased for the respective photosensitizers **BDPY-DBPMB** and **NBDPY-DBPMB**. Based on the present work, further efforts to design and develop NIR BODIPY photosensitizers with hydrophilic functional group and multi-functional applications such as PDT, luminescent bioimaging and fluorescent sensor materials, are underway in our lab.

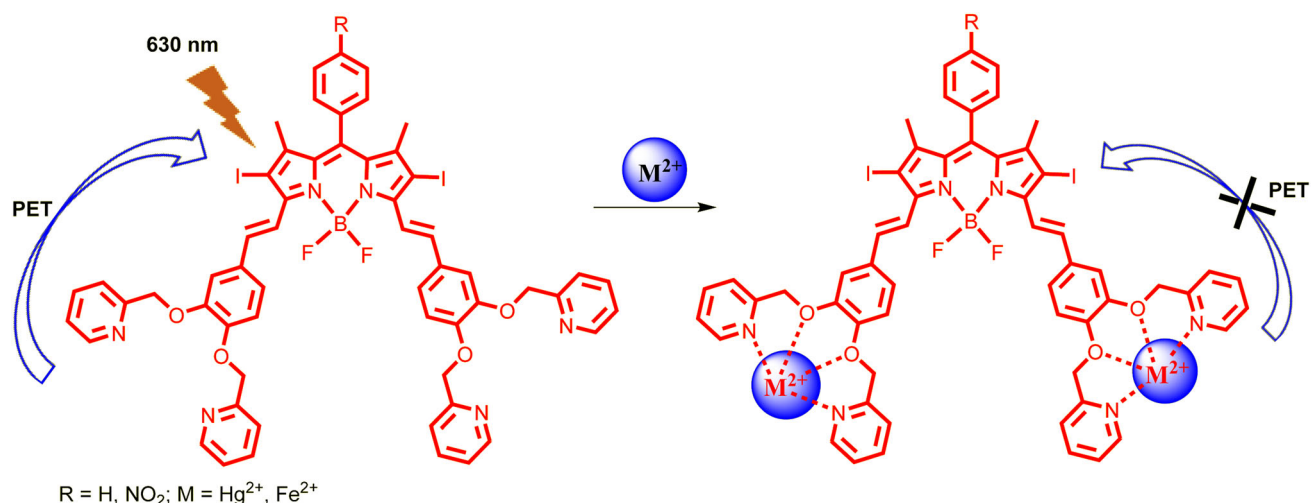


Figure 6. Probable binding mechanism of photosensitizers **BDPY-DBPMB** and **NBDPY-DBPMB** complexed with Hg²⁺ and Fe²⁺, respectively.

Supplementary Information (SI)

All the characterization spectra and absorption/emission spectra in presence of TFA of **BDPY-DBPMB** and **NBDPY-DBPMB**, ¹O₂ photosensitizing ability of **BDPY-DBPMB** and **NBDPY-DBPMB** in presence of DPBF, and absorption/emission spectra of **BDPY-DBPMB** and **NBDPY-DBPMB** upon addition of various metal ions are given in Figures S1-S11. Supplementary Information is available at www.ias.ac.in/chemsci.

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