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PAPER

Synthesis, characterization, and photophysical properties of novel ball-type dinuclear and mononuclear containing four 1,1'-binaphthyl-8,8'-diol bridged metallophthalocyanines with long triplet state lifetimes[†]

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The syntheses of new ball-type dinuclear Si(IV)(CH₃COO)₂ and Ti(IV)O phthalocyanines and two different mononuclear Zn(II) and Ti(IV)O phthalocyanines containing four 1,1'-binaphthyl-8,8'-diol substituents on the peripheral positions are described. The structures of these compounds were characterized using the elemental analyzes, UV-Vis, FT-IR, ¹H NMR and mass spectroscopies. The $\Phi_{\rm F}$ values are 0.14, 0.10, 0.04, 0.02, 0.07; $\Phi_{\rm T}$ values are 0.69, 0.71, 0.85, 0.33, 0.71 for 7–11, respectively. All complexes showed very long triplet lifetimes with $\tau_{\rm T}$ 7510, 3190, 2880, 2370, 9470 µs for 7–11 in DMSO, respectively.

1. Introduction

Metallophthalocyanines (MPcs) have been the subject of great interest in areas such as molecular electronics,¹ non-linear optics,² liquid crystals,³ gas sensors⁴ and photosensitizers,^{5,6} electrocatalysis,7 semiconductors8 and photovoltaic cells.9 There is considerable interest in MPc complexes containing nontransition metals for use as photosensitizers in the relatively new method of cancer treatment called photodynamic therapy (PDT).^{5,6,10-14} The PDT properties of the phthalocyanines are strongly influenced by the presence of diamagnetic central metal ions such as Mg²⁺, Zn²⁺ and substituents introduced on the periphery of the phthalocyanines. Ball-type Pc derivatives were published in the literature for the first time in 2002.¹⁵ Spectroscopic and electrochemical properties of ball-type phthalocyanine differ significantly from the parent monomer.16 Most studies on balltype phthalocyanines have concentrated on complexes containing Zn and Co as central metals. Studies on ball-type MPc derivatives containing silicon or titanium central metal are still limited and the photophysical properties of these molecules are unknown. In this paper, we synthesized and characterized mononuclear Ti(IV)OPc (7), Zn(II)Pc (8 and 11) and ball-type phthalocyanines containing Ti(IV)O (9) and Si(IV)(CH₃COO)₂ (10) as central metals. The complexes are substituted with four 1,1'-binaphthyl-8,8'-diol at the peripheral (β) position, Scheme 1. In addition, photophysical properties of these complexes are investigated.



Scheme 1 i: DMSO, rt, 2 days for **4**, 4 days for **5** and 7 days for **6**, K₂CO₃; ii: *n*-pentanol, DBU (or urea for **7** and **9**), reflux, overnight, metal salt.

2. Results and discussion

2.1. Synthesis and characterization

4-Nitrophthalonitrile 1 and 1,2-dichloro-4,5-dicyanobenzene 2 were synthesized as reported in the literature.^{17,18} 1,1'-Binaphthyl-8,8'-diol 3 was obtained from commercial suppliers. The synthesis of bisphthalodinitrile 5 is based on the reaction of diol 3 with excess of compound 1. Compounds 4 and 6 are prepared from 3 in the presence of 1 or 2, respectively. The reactions are carried out in dry DMSO in the presence of K₂CO₃ as a base, at room temperature, and good yields were obtained. Cyclotetramerization of the phthalonitrile derivatives 4–6 to the Ti(IV)OPc derivatives (7 and 9) was accomplished by using Ti(IV)butoxide and urea, whereas cyclotetramerization of the phthalonitrile derivative 4, 5 and 6 to the Zn(II)Pc derivatives (8 and 11) and, Si(IV)(CH₃COO)₂Pc derivative

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(10) was accomplished by using in *n*-pentanol in the presence of DBU at the reflux temperature. Column chromatography on silica gel using CHCl₃ as mobile phase was used to purify complexes 4–11. The structure and purity of the Ti, Si and Zn Pc derivatives was confirmed by UV-Vis, ¹H NMR, IR, mass spectral data and elemental analyses.

The IR spectra of **5–10** clearly indicates the absence of OH groups of **3**, The CN vibrational peaks are observed at 2232, 2232 and 2238 cm⁻¹ for compounds **4–6**, respectively. A diagnostic feature of the formation of **7–11** from the phthalodinitrile derivatives **4–6**, is the disappearance of the sharp CN vibration of the latter. The remaining IR spectra were very similar for compounds **4–11** and showed Ar–O–Ar peaks at 1246, 1278, 1276, 1259, 1256, 1255, 1255 and 1254 cm⁻¹, respectively.

¹H NMR spectra of 7–11, recorded in DMSO, were similar to each other and showed complex patterns due to the mixed isomer character of this complexes. The OH protons of 4 are observed as a broad signal around 7.7 ppm and the signal disappeared by deuterium exchange. The aromatic protons appear at 8.20-6.93 ppm integrating for a total of 15 for protons for 4. The ¹H NMR spectra of 5 and 6 show the aromatic protons between 8.20–6.93 and 8.62–7.37 ppm, integrating for a total of 18 and 14 for protons, respectively. Aromatic Pc protons appear between 8.69-7.32, 8.70-7.33 8.22-6.99, 8.20-7.01 and 9.15-6.85 ppm integrating for a total of 56, 56, 72, 84, 64 for 7-11, respectively. In addition, in the ¹H NMR spectrum of 10, the protons belong to axial acetate groups in silicon are observed at 2.30 ppm whereas in the ¹H NMR spectrum of 11, the OH protons are observed as sharp signals around at 9.15 ppm and the signal disappeared by deuterium exchange. These results confirm that the complexes have been synthesized successfully

Elemental analysis results were also consistent with the theoretical values of proposed structures for **4–11**. These analyses gave percentage carbon, hydrogen and nitrogen values that were in 0.3%in all cases, which is within an acceptable range for Pc complexes.

The purified phthalocyanines were further characterized by mass spectra. The expected mass values corresponded with the found values for all complexes. Deprotonated ion peaks were observed for complexes **7**, **8**, **10** and **11**. Complex **9** showed a protonated molecular ion peak. The ion peak of complexes **7–11** were observed at 1704.27, 1705.40, 2281.81, 2443.985 and 1713.51 amu, respectively. These results confirm that the complexes have been synthesized successfully

The UV-Vis spectra in DMSO are shown in Fig. 1, for 7– 11. The Q-band maxima are listed in Table 1 in DMSO. The phthalocyanines show typical electronic spectra with two strong absorption regions, one of them in the UV region between 300– 400 nm (B-band) and the other in the visible region between

Table 1UV-Vis (nm) absorption (Q-band), emission and excitationspectral data, and photophysical data for the phthalocyanines 7–11 inDMSO

Complex	λ_{Abs}	$\lambda_{ m Ems}$	$\lambda_{\rm Exc}$	$\Delta\lambda_{\text{Stokes}}$	${\pmb \Phi}_{ m F}$	$arPsi_{ ext{T}}$	$arPhi_{ m IC}$	$\tau_{\rm T}/\mu{ m s}$
7	701	706	701	5	0.14	0.69	0.17	7510
8	679	690	681	11	0.10	0.71	0.19	3190
9	708	715	710	7	0.04	0.85	0.11	2880
10	709	716	711	2	0.02	0.33	0.65	2370
11	685	694	686	9	0.07	0.71	0.22	9470



Fig. 1 Absorption spectra of complex 7–11 in DMSO at concentration 1.0×10^{-5} mol dm⁻³.

600-750 nm (Q-band) and are characteristic Q band transitions of metallophthalocyanines with D_{4h} .¹⁹ Aggregation behavior of Pc is depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes and it is dependent on concentration, the nature of solvent and substituents, metal ions and temperature.²⁰ Aggregation in MPcs is typified by broadened or split Q-band, with the high energy band being due to the aggregate and the low energy band due to the monomer. The UV-Vis spectra of the ball-type Pcs resemble those of other Pcs but with some differences. The broad shoulder near 644 nm for 9, 618 nm for 10 has been reported to indicate aggregation of complexes of ball-type structure.¹⁶ The absorbance near 640 nm for 7, 614 nm for 8, 619 nm for 11, indicates aggregation for phthalocyanine complexes in general.¹⁹ In Fig. 1, complexes 7-11 show Q-band absorptions of the monomers at 700, 678, 713, 710/677, 685 nm in CHCl₃, whereas these complexes show Q-band absorption at 701, 679, 708, 709, 685 nm in DMSO in Table 1. Red shifting of the spectra observed in Q-bands of 7 and 9 is due to the electron density enhancement caused by the central metal, typical of TiPc derivatives.²¹ Complexes 7-11 show B-band at 346, 348, 340, 333, and 343 nm in DMSO, respectively. Typical of ball-type phthalocyanines, the intensity of the B bands is high relative to the Q-band. This may be due to intramolecular interactions between the Pc rings for 9 and 10. Ti and Si complexes (7, 9, 10) show a charge transfer band near 420 nm whereas zinc complexes 8 and 11 do not show charge transfer bands. The substituents and the distance between the two Pc units of the ball-type molecule considerably affect the degree of the interaction between the rings. It can be seen from the electronic absorption spectrum of 10 that the Q-band is split into two, with maxima at 680 and 709 nm. The splitting of the Q-band could be attributed to molecular distortion as well as stronger intramolecular interactions,¹⁸ which are expected to contribute towards the splitting of the Q-band by lowering of the symmetry. Splitting of the Q-bands may also be interpreted in terms of the interactions between the highest occupied molecular orbitals (HOMOs) of the two Pc rings. Although the Q-band in the electronic spectrum of 9 is not split, a well-defined absorption at 709 with an intense absorption at 644 and 680 nm can be attributed to intramolecular interactions.

2.2. Fluorescence spectra and quantum yields

The absorption and fluorescence excitation spectra of complexes **7–11** in DMSO are shown in Fig. 2. The excitation, absorption and emission spectral data are listed in Table 1. All complexes showed similar fluorescence behavior, the absorption and excitation



Fig. 2 Absorbance (a), excitation (b), emission (c) spectra of complex 7–11 in DMSO. Excitation $\lambda_{max} = 621, 609, 615, 611$ and 611 nm, respectively.

spectra show the same Q-band maxima, however, they are broadened compared to emission spectra due to aggregation. The proximity of the wavelength of each component of the Q-band absorption to the Q-band maxima of the excitation spectra for all complexes suggest that the nuclear configurations of the ground and excited states are similar and not affected by excitation. The emission peak is narrower since aggregates are not known to fluoresce. Stokes' shifts range from 2 to 11 nm for **7–11**, and are typical of MPc complexes.²²

The fluorescence quantum yield $(\Phi_{\rm F})$ values are typical of MPc complexes. The $\Phi_{\rm F}$ values are 0.14, 0.10, 0.04, 0.02, 0.07 in DMSO for 7–11, respectively. The $\Phi_{\rm F}$ values were lower for ball-type derivative than for other derivatives, which are peripherally substituted. This is attributed to the ball-type structure for 9 and 10 which may encourage intersystem crossing to the triplet state due to its larger size, as will be confirmed below.

2.3. Triplet quantum yields and lifetimes

The triplet quantum yields (Φ_T) and lifetimes of the complexes are listed in Table 1 and Fig. 3 shows a representative triplet decay curve for complex **10** as an example (see Suppl. Material for the rest of the complexes[†]).



Fig. 3 Decay curves of complex 10.

Second order kinetics were obeyed by all complexes. This is typical of MPc complexes at high concentrations ~ 10^{-5} M or higher due to triplet–triplet recombination.²³ The concentrations employed in this work were in this range hence triplet–triplet recombination is expected.

Triplet quantum yield Φ_{T} represents the fraction of absorbing molecules that undergo intersystem crossing to the metastable triplet excited state. Therefore, factors which induce spin–orbit coupling will certainly populate the triplet excited state.

High $\Phi_{\rm T}$ values and correspondingly low $\Phi_{\rm F}$ values for MPc derivatives under discussion, suggest more efficient intersystem crossing (ISC). The $\Phi_{\rm T}$ values for **7–11** are 0.69, 0.71, 0.85, 0.33, 0.71 respectively. The high values of $\Phi_{\rm T}$ for complex **9** when compared to complex **7** are accounted for by the ball-type structure which will encourage intersystem crossing, resulting in larger $\Phi_{\rm T}$ and correspondingly lower $\Phi_{\rm F}$ values as discussed above. Complex **10** with a low $\Phi_{\rm F}$ value also has a low $\Phi_{\rm T}$ value, suggesting loss of energy by non-radiative means.

Complexes 7–11 (except 10) have the low Φ_{IC} values, showing minimal loss of energy by non-radiative decay from the excited singlet state. The complexes showed reasonably long triplet lifetimes with $\tau_{\rm T}$ 7510, 3190, 2880, 2370, 9470 µs, respectively. These are longer triplet lifetimes than normal for phthalocyanines,²² hence show that these complexes have an excellent potential as photosensitizers. The $\tau_{\rm T}$ values for ball-type phthalocyanines are generally lower than for the corresponding mononuclear derivatives (compare 7 and 9), probably due to self quenching of the rings in the former. The $\tau_{\rm T}$ values for the complexes are very long (in the ms range) compared to phthalocyanines in general.²² These are indeed the longest triplet lifetimes ever reported for phthalocyanine complexes.^{24,25} Triplet lifetime values of near 40 µs were obtained for phenoxy or benzyloxy tetrasubstituted oxotitanium phthalocyanines. For ZnPc derivatives tetrasubstituted with pyridyloxy, the triplet lifetimes were 7 µs in DMF and 350 µs in DMSO. MPc complexes with $\tau_{\rm T}$ of ~ 1.5 ms are known,²⁵ but the values reported here are much longer ranging from ~ 2.4 to 9.5 ms.

3. Experimental

3.1 Materials

Silicon(IV) tetraacetate, titanium(IV) butoxide and zinc(II) acetate were purchased form Sigma–Aldrich. Dimethylsulfoxide (DMSO), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), dimethylformamide (DMF), dichloromethane (DCM) and chloroform were purchased from Saarchem. Silica gel for column chromatography was purchased from MERCK. All other reagents were obtained from commercial suppliers and used as received. All solvents were dried and purified as described by Perrin and Armarego.²⁶

3.2 Equipment

UV-Vis absorption spectra were obtained using the Varian Cary 500 UV-Vis/NIR spectrophotometer. Fluorescence excitation and emission spectra were recorded with a Varian Eclipse spectrophotometer. FT-IR data (ATR) were recorded using the Perkin–Elmer spectrum 100 FTIR spectrometer. ¹H NMR spectra were obtained using a Bruker EMX 400 MHz spectrometer. Elemental analysis were done on a Finnigan Flash EA 1112 Series Elementar. Mass spectra data were collected with a Bruker AutoFLEX III Smartbeam MALDI TOF/TOF Mass spectrometer. The instrument was operated in positive ion mode using a m/z range of 400–3000. The voltage of the ion sources were set at 19 and 16.7 kV for ion sources 1 and 2, respectively, while the lens was set at 8.50 kV. The reflector 1 and 2 voltages were set at 21 and 9.7 kV, respectively. The spectra were acquired using dithranol as the MALDI matrix, using a 354 nm nitrogen laser.

Triplet absorption and decay kinetics were recorded on a laser flash photolysis system, the excitation pulses were produced by a Quanta-Ray Nd: YAG laser providing 400 mJ, 9 ns pulses of laser light at 10 Hz, pumping a Lambda-Physik FL 3002, dye (Pyridin 1 in methanol). The analyzing beam source was from a Thermo Oriel xenon arc lamp, and a photomultiplier tube was used as a detector. Signals were recorded with a two-channel 300 MHz digital real-time oscilloscope (Tektronix TDS 3032C); kinetic curves were averaged over 256 laser pulses. The triplet lifetimes were determined by exponential fitting of the kinetic curves using the program OriginPro 7.1.

3.3 Synthesis

The target precursors were prepared by a nucleophilic aromatic substitution reaction between 4-nitrophthalonitrile 1 or 1,2-dichloro-4,5-dicyanobenzene 2 and 1,1'-binaphthyl-8,8'-diol 3, Scheme 1.

3.3.1. General Procedure for 4-6. Compound 3 (3.31 g, 11.55 mmol) was dissolved in dry DMSO (15 mL) and 1 (2 g, 11.55 mmol for 4, 4 g, 23.1 mmol for 5), or 2 (1.0 g, 5.1 mmol for 6) was added under inert atmosphere. To this reaction mixture, finely ground anhydrous potassium carbonate (1.60 g, 11.55 mmol for 4, 3.2 g, 23.00 mmol for 5, 2.8 g, 20.3 mmol for 6) was added. After 4 h of stirring at room temperature, further potassium carbonate (0.40 g, 2.88 mmol for 4, 0.79 g, 5.8 mmol for 5, 0.70 g, 5.1 mmol for 6) was added and this same amount was added again after 24 h of stirring. After a total of 48 h, 96 h and 7 days of stirring, for 4, 5 and 6, respectively, the reaction mixture was poured into water (50, 50 and 175 mL) resulting in the formation of light yellow precipitates for 4-6, respectively. The crude product was centrifuged and was further purified by chromatography over a silica gel column using a CHCl₃ as eluent. The product was recrystallized from ethanol and then the pure product was dried using P_2O_5 for two weeks.

4-(8'-Hydroxy-1,1'-binaphthyl-8-yloxy)phthalonitrile (4). The product is white in colour. Yield: 2.0 g, 42%. Mp. 113 °C. IR (KBr) (v_{max} /cm⁻¹): 3465 (Ar–OH), 3054 (Ar–CH), 2232 (C=N), 1586 (C=C), 1246 (C–O–C). ¹H NMR (DMSO- d_6): δ , ppm 8.20 (2H, d, J = 9.2 Hz, Ar–H), 8.08 (1H, d, J = 8.0 Hz, Ar–H), 7.85 (2H, d, J = 8.4 Hz, Ar–H), 7.70 (1H, b, OH), 7.55 (2H, t, J = 7.4 Hz, Ar–H), 7.48 (2H, d, J = 7.2 Hz Ar–H), 7.46 (1H, s, Ar–H), 7.38 (2H, t, J = 7.4 Hz, Ar–H), 7.16 (1H, d, J = 8.0 Hz, Ar–H), 6.93 (2H, d, J = 7.6 Hz, Ar–H). Calcd for C₂₈H₁₅N₂O₂: C, 81.54; H, 3.91; N, 6.79%. Found: C, 81.48; H, 3.91; N, 6.80%. MS m/z Calculated: 412.12. Found [M]⁺: 412.37.

4,4'-(1,1'-Binaphthyl-8,8'-diylbis(oxy))diphthalonitrile (5). A light yellow solid was obtained. Yield: 2.1 g, 34%. Mp. 150 °C. IR (KBr) (v_{max} /cm⁻¹): 3072 (Ar–CH), 2232 (C==N), 1586 (C==C), 1278 (C–O–C). ¹H NMR (DMSO- d_6): δ , ppm 8.20 (2H, d, J = 8.8 Hz, Ar–H), 8.08 (2H, d, J = 8.4 Hz, Ar–H), 7.85 (2H, d, J = 8.8 Hz, Ar–H), 7.55 (2H, t, J = 7.8 Hz, Ar–H), 7.49 (2H, s, Ar–H), 7.39 (2H, t, J = 7.2 Hz, Ar–H), 7.30 (2H, d, J = 8.4 Hz, Ar–H), 7.16 (2H, d, J = 8.0 Hz, Ar–H), 6.93 (2H, d, J = 8.4 Hz, Ar–H). Calcd for C₃₆H₁₈N₄O₂: C, 80.29; H, 3.37; N,10.40%. Found: C, 80.24; H, 3.37; N, 10.37%. MS *m*/*z* Calculated: 538.55. Found [M]⁺: 538.0.

4,5-(1,1'-Binaphthyl-8,8'-diyldi(oxy)phthalonitrile (6). A white solid was obtained. Yield: 1.2 g, 20%. IR (KBr) (v_{max}/cm^{-1}): 3085 (Ar–CH), 2238 (C=N), 1577 (C=C), 1276 (C–O–C). ¹H NMR (DMSO- d_6): δ , ppm 8.62 (2H, s, Ar–H), 8.23 (2H, d, J = 9.2 Hz, Ar–H), 8.13 (2H, d, J = 8.0 Hz Ar–H), 7.67 (2H, d, J = 8.8 Hz Ar–H), 7.61 (2H, t, J = 8.4 Hz Ar–H), 7.51 (2H, t, J = 8.4 Hz Ar–H), 7.37 (2H, d, J = 8.4 Hz Ar–H). Calcd for C₂₈H₁₄N₂O₂: C, 81.94; H, 3.44; N, 6.83%. Found: C, 81.99; H, 3.45; N, 6.84%. MS m/z Calculated: 410.42. Found [M]⁺: 410.12.

3.3.2. General procedure for 7–11. A mixture of complex 4–6 (0.500 g, 1.21 mmoL for 4, 1.22 mmoL for 5, 0.93 mmoL for 6),

titanium(IV)butoxide (0.51 mL, 1.5 mmoL for 7 and 9) and urea (0.072 g, 1.21 mmoL for 7 and 9), zinc(II)acetate (0.50 g, 0.30 mmoL for 8 and 11) silicon(IV)acetate (0.32 g, 1.21 mmoL for 10) and 10 drops DBU were dissolved in dried n-pentanol (7 mL). After heating, an excess of titanium(IV)butoxide and silicon(IV)acetate was added again for 9 and 10. The reaction mixture was heated with stirring at 140 °C under nitrogen overnight. After cooling to room temperature, methanol (100 mL) was added to the reaction mixture followed by heating at reflux temperature to precipitate the product. After cooling to room temperature, the precipitate was filtered and washed with methanol and water several times and finally washed with methanol, ethanol, acetonitrile and acetone for 24 h, consecutively in the Soxhlet apparatus. Then, each of the dark colored phthalocyanine derivatives were separated by chromatography on silica gel column using chloroform (twice) as eluent. Finally, the dark green titanium, silicon and zinc phthalocyanines were dried using P_2O_5 for 10 days. All of these compounds are soluble in common solvents such as CHCl₃, DCM, DMF and DMSO, which have a $Mp > 350 \,^{\circ}C.$

2,3,9,10,16,17,23,24-Octakis(1,1'-binaphthyl-8,8'-diyldi(oxy)phthalocyaninatooxo titanium(tv) (7). Yield: 0.158 g, 7.6%. Dark green colour. UV-Vis (CHCl₃) λ_{max} /nm (log ε /dm⁻³ mol⁻¹ cm⁻¹): 700 (5.09), 666 (4.79), 635 (4.68), 342 (4.94). IR [(KBr) ν_{max} /cm⁻¹]: 3086 (Ar–CH), 1579 (C=C), 1259 (C–O–C). ¹H NMR (DMSO-*d*₆): δ , ppm 8.69–7.32 (56H, m, Ar–H). Anal. calcd. for C₁₁₂H₅₆N₈O₉Ti: C, 78.87; H, 3.31; N, 6.57. Found: C, 78.91; H, 3.30; N, 6.57%. MALDI-TOF-MS *m*/*z* Calculated: 1705.56. Found [M – H]⁺: 1704.27.

2,3,9,10,16,17,23,24-Octakis(1,1'-binaphthyl-8,8'-diyldi(oxy)phthalocyaninatozinc(II) (8). Yield: 0.158 g, 7.6%. Green colour. UV-Vis (CHCl₃) λ_{max} /nm (log ε /dm⁻³ mol⁻¹ cm⁻¹): 678 (5.11), 350 (4.80). IR [(KBr) v_{max} /cm⁻¹]: 3085 (Ar–CH), 1580 (C==C), 1256 (C–O–C). ¹H NMR (DMSO- d_6): δ , ppm 8.70–7.33 (56H, m, Ar–H). Anal. calcd. for C₁₁₂H₅₆N₈O₈Zn: C, 78.80; H, 3.31; N, 6.56. Found: C, 78.79; H, 3.31; N, 6.55%. MALDI-TOF-MS *m/z* Calculated: 1707.10. Found [M – 2H]⁺: 1705.40.

2',10',16',24'-[Tetrakis(4,4'-(1,1'-binaphthyl-8,8'-diyl(oxy)) diphenyl)]bis-phthalocyaninatodioxotitanium(IV) (9). Yield: 0.112 g, 5.3%. Dark green colour. UV-Vis (CHCl₃) λ_{max} /nm (log ε /dm⁻³ mol⁻¹ cm⁻¹): 713 (5.18), 679 (4.86), 646 (4.70), 331 (5.47). IR [(KBr) v_{max} /cm⁻¹]: 3084 (Ar–CH), 1578 (C=C), 1255 (C–O–C). ¹H NMR (DMSO-*d*₆): δ , ppm 8.22–7.12 (64H, m, Ar'–H), 6.99 (8H, d, Ar–H). Anal. calcd. for C₁₄₄H₇₂N₁₆O₁₀Ti₂: C, 75.79; H, 3.18; N, 9.82. Found: C, 75.80, H, 3.17; N, 9.79%. MALDI-TOF-MS *m*/*z* Calculated: 2281.95. Found [M]⁺: 2281.81.

2',10',16',24'-[Tetrakis(4,4'-(1,1'-binaphthyl-8,8'-diyl(oxy)) diphenyl)]bis-hthalocyaninatodisilicon(IV)diacetate (10). Yield: 0.102 g, 4.5%. Open green-blue colour. UV-Vis (CHCl₃) λ_{max}/nm (log ε/dm^{-3} mol⁻¹ cm⁻¹): 710 (4.62), 677 (4.68), 645 (4.53), 616 (4.38), 408 (4.28). IR[(KBr) v_{max}/cm^{-1}]: 3085 (Ar–CH), 1580 (C=C), 1255 (C–O–C). ¹H NMR (DMSO- d_6): δ , ppm 8.20–7.10 (64H, m, Ar–H), 7.01 (8H, d, Ar–H), 2.30 (12H, s, CH₃). Anal. calcd. for C₁₅₂H₈₄N₁₆O₁₆Si₂: C, 74.62; H, 3.46; N, 9.16. Found: C, 74.61; H, 3.45; N, 9.18%. MALDI-TOF-MS *m/z* Calculated: 2446.56. Found [M – 2H]⁺: 2443.98.

(4)-Tetra(1,1'-binaphtoxy)phthalocyaninatozinc(II) (11). Yield: 0.128 g, 6.2%. Green colour. UV-Vis (CHCI₃) λ_{max} /nm (log ε /dm mol⁻¹ cm⁻¹): 685 (4.79), 332 (4.76). IR [(KBr) v_{max} /cm⁻¹]: 3415 (Ar–OH), 1254 (C–O–C). ¹H NMR (DMSO): δ = 7.98–7.04 (52H, m, Ar–H), 9.15 (4H, s, Ar–OH), 6.85 (8H, d, Ar–H in R group). Anal. calcd. for C₁₁₂H₆₄N₈O₈Zn: C, 78.43; H, 3.76; N, 6.53. Found: C, 78.45; H, 3.75; N, 6.53%. MALDI-TOF-MS *m*/*z* Calc: 1715.17. Found [M – 2H]⁺: 1713.51.

3.4. Photophysical Studies

3.4.1 Fluorescence quantum yields. Fluorescence quantum yields ($\Phi_{\rm F}$) were determined by the comparative method,^{27,28} eqn (1):

$$\Phi_{\rm F} = \Phi_{\rm F(Std)} \frac{F.A_{\rm Std} \, n^2}{F_{\rm Std} \, A_{\rm Std}^2} \tag{1}$$

where *F* and *F*_{std} are the areas under the fluorescence curves of **7–11** and the standard, respectively. *A* and *A*_{std} are the respective absorbances of the sample and standard at the excitation wavelengths (which was ~0.05 in all solvents used), and *n* and *n*_{std} are the refractive indices of solvents used for the sample and standard, respectively. ZnPc ($\Phi_{\rm F} = 0.20$) was employed as the standard.²⁹

3.4.2 Triplet quantum yields and lifetime. The solutions for triplet quantum yields and lifetimes were introduced into a 10 mm pathlength UV-Visible spectrophotometric cell, deaerated using nitrogen and irradiated at the Q-band maxima. Triplet state quantum yields (Φ_T) of 7–11 were determined by the triplet absorption method,³⁰ using zinc phthalocyanine (ZnPc) as a standard, eqn (2):

$$\Phi_{\rm T} = \Phi_{\rm T}^{\rm Std} \cdot \frac{\Delta A_{\rm T} \cdot \mathcal{E}_{\rm T}^{\rm Std}}{\Delta A_{\rm T}^{\rm Std} \cdot \mathcal{E}_{\rm T}}$$
(2)

where $\Delta A_{\rm T}$ and $\Delta A_{\rm T}^{\rm Std}$ are the changes in the triplet state absorbances of **7–11** and the standard, respectively. $\varepsilon_{\rm T}$ and $\varepsilon_{\rm T}^{\rm Std}$ are the triplet state molar extinction coefficients for **7–11** and the standard, respectively. $\Phi_{\rm T}^{\rm Std}$ is the triplet quantum yield for the standard, ZnPc ($\Phi_{\rm T} = 0.65$ in DMSO).³¹ $\varepsilon_{\rm T}$ and $\varepsilon_{\rm T}^{\rm Std}$ were determined from the molar extinction coefficients of their respective ground singlet state ($\varepsilon_{\rm S}$ and $\varepsilon_{\rm S}^{\rm Std}$) and the changes in absorbances of the ground singlet states ($\Delta A_{\rm S}$ and $\Delta A_{\rm S}^{\rm Std}$) and excited triplet states ($\Delta A_{\rm T}$ and $\Delta A_{\rm T}^{\rm Std}$) according to eqn (3):

$$\varepsilon_{\rm T} = \varepsilon_{\rm S} \cdot \frac{\Delta A_{\rm T}}{\Delta A_{\rm S}} \tag{3}$$

Quantum yields of internal conversion (Φ_{IC}) were obtained from eqn (4), which assumes that only three processes (fluorescence, intersystem crossing and internal conversion), jointly deactivate the excited singlet state of complexes 7–11.

$$\Phi_{\rm IC} = 1 - (\Phi_{\rm F} + \Phi_{\rm T}) \tag{4}$$

Conclusions

We report on the synthesis and photophysical properties of balltype and monuclear 1,1'-binaphthyl-8,8'-diol substitued Si, Zn and Ti Pc complexes. Elemental analyses, IR, ¹H NMR, UV-Vis and

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