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## PAPER



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# Synthesis, characterization, third-order non-linear optical properties and DFT studies of novel SUBO bridged ball-type metallophthalocyanines<sup>†</sup>

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Novel 4,4'-(((2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diyl)bis(2-methylpropane-2,1-diyl))bis(oxy)) (SUBO) bridged ball-type metallophthalocyanines were synthesized starting from 4,4'-(((2,4,8,10-tetraoxaspiro[5.5] undecane-3,9-diyl)bis(2-methylpropane-2,1-diyl))bis(oxy))diphthalonitrile with convenient metal salts in 2-N,N-dimethylaminoethanol. A new bisphthalonitrile compound was obtained from 2,2'-(2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diyl)bis(2-methylpropan-1-ol) and 4-nitrophthalonitrile in acetonitrile at reflux temperature in the presence of potassium carbonate as a catalyst. The structural characterization of the compounds was performed by elemental analysis, and infrared, ultraviolet-visible and matrix-assisted laser desorption/ionization time-of-flight mass spectroscopic methods. Nonlinear absorptions of the phthalocyanine complexes were measured using the Z-scan technique with 7 ns pulse duration at a 532 nm wavelength. It is obvious that ball-type copperphthalocyanine has a high nonlinear absorption coefficient and imaginary component of the third-order susceptibility compared to other complexes. Therefore, ball-type copperphthalocyanine can be regarded as a very good candidate for optical limiting applications. Density functional theory was used for geometry optimizations and time-dependent density functional theory calculations of electronic transitions in order to compare with the experimental results. Molecular orbital and nonlinear optical analyses were also performed with density functional theory at the CAM-B3LYP/6-31G(d,p)/ LANL2DZ level. The nonlinear optical analyses show that ball-type copperphthalocyanine has significantly better nonlinear optical properties in comparison to a common reference compound, urea.

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## 1. Introduction

Phthalocyanines (Pcs) include an electron rich macrocycle facilitating the substitution of different groups and coordinating many transition metal ions at the centre of the macroring which leads to important effects on the chemical and physical properties of phthalocyanines.<sup>1–5</sup>

Nowadays, a new class of phthalocyanines called ball-type phthalocyanines (BTPcs) which were first introduced by our

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<sup>e</sup>Hacettepe University, Chemistry Department, 06800 BeytepeAnkara, Turkey. E-mail: bekir@hacettepe.edu.tr group have attracted much more interest from researchers than their mono-type sorts.<sup>6–8</sup> These complex molecules accommodate two macrorings containing an 18  $\pi$  electronic system connected to each other with four bridges and have a face-to-face structure which affects their behaviour substantially.<sup>7,9</sup>

Due to their different structure from the mono-type family, ball-type phthalocyanines show interesting properties for various applications like non-linear optics,<sup>10–13</sup> gas sensors<sup>6,14–16</sup> and catalysis.<sup>7,9,17,18</sup>

Over the past few decades, studies on the nonlinear optical (NLO) properties of materials for optical limiting (OL) have been focused on novel organic materials to protect human eyes and sensitive photonic devices from laser damage due to the exposure to high intensity laser light.<sup>19</sup> With tuning of the factors affecting the nonlinear behaviour such as the ease of processability, the identity of insertion metal ions, the substitution of long and bulky groups at peripheral/non-peripheral positions, and changing the symmetry of the macrocycle, it is possible to enrich the nonlinear response and optical limiting performance using phthalocyanines and their derivatives.<sup>20–23</sup>

To the best our knowledge, the OL properties of the studied SUBO bridged BTMPc have not been reported to date, even

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though a lot of work has been done on the nonlinear optical parameters of other Pc complexes. Hence, this study was devoted to the investigation of the nature of the nonlinear behaviour of the SUBO bridged BTMPc to bring clarity to the influencing factors mentioned above.

Inspired by the unique structure, the adaptable bridge distance between their two planes and therefore the flexibility in the synthesis of ball-type metallophthalocyanines, 4,4'-(((2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diyl)bis(2-methyl propane-2,1-diyl))bis(oxy)) (SUBO) bridged ball-type metallophthalocyanines with transition metal centres have been synthesized and characterized with elemental analysis, and FTIR, <sup>1</sup>H-NMR and MALDI TOF mass spectroscopy methods. To the best of our knowledge, no study has been conducted on the synthesis and characterization of these kinds of complexes bearing four SUBO bridges.

A Z-scan open aperture setup is constructed for the nonlinear optical characterization of the synthesized complexes. The basic Z-scan system is powered by a Q-switch Nd:YAG nanosecond pulsed laser (Solar Systems LPS1500, 20 Hz repetition rate, 7 ns pulse duration, and 110 mJ output energy) and includes a Si-photodetector, a spatial filter for Gaussian beam profile and all other required optical apparatus.

In addition, the proposed geometries of the compounds were confirmed by computational methods.

### 2. Experimental

#### 2.1. Materials and methods

IR and electronic spectra were measured on a Shimadzu FTIR-8300 (ATR and KBr pellets) and a Shimadzu UV-2600 UV-VIS spectrophotometer, respectively. Elemental analyses were accomplished using a CHNS-932 (LECO). Mass spectra were acquired using a Rapiflex MALDI-TOF-MS (Bruker Daltonics, Bremen-GERMANY) equipped with a Smartbeam 3D 10 kHz 355 nm Nd:YAG laser applying 2000 laser shots per sample spot using a single shot laser configuration. All MALDI-TOF-MS data were acquired in positive ion and reflectron modes. Calibration was performed with a series of peptides existing in a mixture (Bruker Daltonics standard) prior to mass spectrometric analysis of the samples.

The <sup>1</sup>H-NMR and <sup>1</sup>H–<sup>1</sup>H COSY-NMR spectra of the compounds were obtained using a Varian Mercury 400 MHz NMR spectrometer, Agilent Technologies with TMS as an internal standard.

#### 2.2. MALDI TOF MS measurements

**2.2.1 Sample preparation.** For the samples, 1 mg of each sample was dissolved in 1 mL of an ACN–DMSO–H<sub>2</sub>O mixture solution (50:2:48, v/v/v) and acidified with 0.2% trifluoro-acetic acid. About 10 mg of the 2,5-dihydroxybenzoic acid MALDI matrix was dissolved in 1 mL of an ACN–DMSO–H<sub>2</sub>O mixture solution (50:2:48, v/v/v) and acidified with 0.2% trifluoroacetic acid. The sample solution was mixed with the matrix solution in a 1:5 volume ratio. Finally, 0.5 µL of the final sample

solution was deposited onto the sample plate dried at room temperature and then analyzed by mass spectrometry.

#### 2.3. Synthesis

2.3.1. Synthesis of the bisphthalonitrile compound (1) (Scheme 1). A mixture of 1.82 g of (6.0 mmol) 2,2'-(2,4,8,10tetraoxa spiro [5.5]undecane-3,9-diyl)bis(2-methylpropan-1-ol) or spirogylicol (SPG), 2.07 g of (12 mmol) 4-nitrophthalonitrile and 4.96 g of (36 mmol) K<sub>2</sub>CO<sub>3</sub> was refluxed in acetonitrile (35 ml) with magnetic stirring in a 100 ml round bottomed flask for 72 h. The cooled reaction mixture was poured into iced water (250 ml) and stirred overnight. The light green precipitate was filtered off and washed with water until the filtrate became neutral, and dried in a vacuum oven at 105 °C. The crude product was separated by column and thin layer chromatography with silica gel using a chloroform/methanol (2.0/0.2) (v/v) system as an eluent. This white colored compound 1 is readily soluble in common organic solvents such as THF, MeOH, EtOH, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> and acetone. Yield:2.83 g (85%), m.p.214 °C. Anal. calcd for C<sub>31</sub>H<sub>32</sub>N<sub>4</sub>O<sub>6</sub>: C, 66.89; H, 5.79; N, 10.07. Found: C, 66.73; H, 5.81; N, 10.11%; IR (ATR)  $\bar{\nu}$ , cm<sup>-1</sup>: 3084 (arom CH), 2918-2849 (aliph CH), 2230 (C=N), 1596–1461 (C=C), 1252 (C–O–C). <sup>1</sup>H-NMR  $\delta$ , (CDCl<sub>3</sub>): 1.05(d, J = 3.08 Hz, 12H, -CH<sub>3</sub> aliph-H<sub>1</sub>), 3.33 (d, J = 11.59 Hz, 2H,  $-CH_2$ - aliph-H<sub>2</sub>), 3.50 (d, J = 11.55 Hz, 2H,  $-CH_2$ - aliph-H<sub>3</sub>), 3.57 (d, J = 11.25 Hz, 2H,  $-CH_2$ - aliph-H<sub>4</sub>), 4.48 (d, J = 11.28Hz, 2H, -CH<sub>2</sub>- aliph-H<sub>7</sub>), 3.83 (d, J = 8.65 Hz, 2H, -CH<sub>2</sub>- aliph-



M: Zn(2), Co(3), Cu(4)

Scheme 1 (i) K<sub>2</sub>CO<sub>3</sub>, AcCN, reflux; (ii) metal(II) acetates, DMAE, 300 °C.

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H<sub>5</sub>), 3.87 (d, J = 8.64 Hz, 2H,  $-CH_2-$  aliph-H<sub>5</sub>), 4.36 (s, 2H, >CH- aliph-H<sub>6</sub>), 7.17 (dd, J = 8.78 Hz, J = 2.59 Hz, 2H, Ar-H<sub>8</sub>), 7.26 (d, J = 2.65 Hz, 2H, Ar-H<sub>9</sub>), 7.68 (d, 2H, Ar-H<sub>10</sub>) (Scheme 1 and Fig. 1–4).

2.3.2. [2,10,16,24-{Tetrakis-4,4'-(((2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-divl)bis(2-methylpropane-2,1-divl))bis(oxy))}diphthalocyaninato-dizinc(II)] (BTZnPc) (2) (Scheme 1). A mixture of 0.20 g of (0.36 mmol) 4,4'-(((2,4,8,10-tetraoxaspiro-[5.5]undecane-3,9-diyl)bis(2-methylpropane-2,1-diyl))bis(oxy))diphthalonitrile (1), 0.039 g of (0.18 mmol) Zn(CH<sub>3</sub>COO)<sub>2</sub>. 2H<sub>2</sub>O and 2 ml of 2-(N,N-dimethilamino)etanol (DMAE) was heated in a vacuum-sealed glass tube for 8 hours at 300 °C. After cooling to room temperature, the reaction mixture was precipitated by pouring it into acetone. Following filtration of the precipitate, it was washed with hot water, methanol, and acetone in the Soxhlet apparatus for 24 hours, respectively. The purification of the crude product was carried out by dissolving it in about 2 ml of DMF and then reprecipitating with the addition of acetone. BTZnPc 2 which is dark green in color is slightly soluble in DMF and DMSO. Mp > 300 °C. Yield: 0.14 g (66%), Anal. calcd for C124H128N16O24Zn2: C, 63.18; H, 5.47; N, 9.51%. Found: C, 63.25; H, 5.45; N, 9.53%. IR (ATR)  $\bar{\nu}$ , cm<sup>-1</sup>: 3075 (arom C-H), 2926-2849 (aliph C-H), 1606-1486 (C=C), 1342 (C-H bend), 1227 (C–O–C). UV-vis, (DMF)  $\lambda_{max}$  (log  $\varepsilon$ ) (nm): 683 (5.19), 647 (4.96), 353 (5.10). MS (MALDI-TOF), m/z: 2353.77  $[M]^+$ (Scheme 1, Fig. 4 and 5(a)).



Fig. 1 <sup>1</sup>H NMR spectrum of bisphthalonitrile compound 1.



Fig. 2 COSY <sup>1</sup>H–<sup>1</sup>H NMR spectrum of bisphthalonitrile compound **1**.

2.3.3. [2,10,16,24-{Tetrakis-4,4'-(((2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diyl)bis(2-methylpropane-2,1-diyl))bis(oxy))}diphthalocyaninato-dicobalt(II)] (BTCoPc) (3) (Scheme 1). A mixture of 0.20 g of (0.36 mmol) 4,4'-(((2,4,8,10-tetraoxaspiro-[5.5]undecane-3,9-diyl)bis(2-methylpropane-2,1-diyl))bis(oxy))diphthalonitrile (1), 0.045 g of (0.18 mmol) Co(CH<sub>3</sub>COO)<sub>2</sub>. 4H<sub>2</sub>O and 2 ml of DMAE was heated in a vacuum-packed glass tube at 300 °C for 8 h. The separation of 3 was achieved by the same way used for 2. The crude metallophthalocyanine, 3, was isolated by the same way as the purification method of the BTZnPc complex. BTCoPc 3 with dark blue color is slightly soluble in DMF and DMSO. Mp >  $300 \, ^{\circ}$ C. Yield: 0.12 g (57%). Anal. calcd for C<sub>124</sub>H<sub>128</sub>N<sub>16</sub>O<sub>24</sub>Co<sub>2</sub>: C, 63.53; H, 5.50; N, 9.56%. Found: C, 63.57; H, 5.53; N, 9.51%. IR (ATR)  $\bar{\nu}$ , cm<sup>-1</sup>: 3073 (arom C-H), 2914-2849 (aliph C-H), 1610-1468 (C=C), 1344 (C–H bend), 1233 (C–O–C). UV-vis, (DMF)  $\lambda_{max} (\log \varepsilon)$  (nm): 670 (4.57), 630 (4.52), 330 (4.83). MS (MALDI-TOF), m/z: 2343.79  $[M]^+$  (Scheme 1, Fig. 4 and 5(b)).

2.3.4. [2,10,16,24-{Tetrakis-4,4'-(((2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diyl)bis(2-methylpropane-2,1-diyl))bis(oxy))}diphthalocyaninato-dicopper(II)] (BTCuPc) (4) (Scheme 1). A mixture of 0.2 g of (0.36 mmol) 4,4'-(((2,4,8,10-tetraoxaspiro-[5.5]undecane-3,9-diyl)bis(2-methylpropane-2,1-diyl))bis(oxy))diphthalonitrile (1), 0.044 g of (0.18 mmol) Cu(CH<sub>3</sub>COO)<sub>2</sub>. XH<sub>2</sub>O and 2 ml of DMAE was heated in a sealed glass tube at 300 °C for 8 h. The same purification technique of complexes 2 and 3 was applied to complex 4. BTCuPc 4 which is dark blue in color is slightly soluble in DMF and DMSO. Mp > 300 °C. Yield: 0.095 g (45%). Anal. calcd for C<sub>124</sub>H<sub>128</sub>N<sub>16</sub>O<sub>24</sub>Cu<sub>2</sub>: C, 63.28; H, 5.48; N, 9.52%. Found: C, 63.45; H, 5.50; N, 9.54%. IR (ATR)  $\bar{\nu}$ , cm<sup>-1</sup>: 3076 (arom C-H), 2924–2853 (aliph C-H), 1611–1466 (C=C), 1338 (C-H bending), 1233 (C-O-C). UV-vis, (DMF)  $\lambda_{max}$  $(\log \varepsilon)$  (nm): 672 (4.46), 632 (4.54), 331 (4.75). MS (MALDI-TOF), m/z: 2351.77[M]<sup>+</sup> (Scheme 1, Fig. 4 and 5(c)).

#### 2.4. Nonlinear optical measurements

For the nonlinear optical characterization of the synthesized complexes, a Z-scan open aperture setup is constructed. The



Fig. 3 UV-vis spectra of BTMPC complexes 2, 3 and 4 in DMF.

system includes the required optical apparatus with a Si-photodetector and is powered by a Q-switch Nd:YAG nanosecond pulsed laser (Solar Systems LPS1500, 20 Hz repetition rate, 7 ns pulse duration, and 110 mJ output energy).

For all the three complexes, the samples are placed one by one inside a quartz cuvette which has a 1 mm optical path. To achieve the Gaussian beam profile, a spatial filter (SF, Thorlabs KT310-M) is placed on the optical path. The corrected beam emerging out of the SF is focused between the two lenses. The intensity of the beam at the focus is measured with a power meter in each separate measurement and implemented in the calculations. While the quartz cuvette passes through the focal point of the front lens, the focused



**Fig. 4** Mass spectra of **2**, **3** and **4** acquired using a Rapiflex MALDI-TOF-MS (Bruker Daltonics, Bremen-GERMANY) equipped with a Smartbeam 3D 10 kHz 355 nm Nd:YAG laser applying 1000 laser shots per sample spot using a single shot laser configuration.

beam interacts with the solution inside the optic cuvette and the Si-detector (Thorlabs-DET36A) detects the transmitted light.

#### 2.5. Computational details

Optimizations in DMF were carried out by using Gaussian09,<sup>24</sup> and Gaussview 5.0 (ref. 25) was used to visualize the UV-Vis spectra and orbitals of the investigated molecules. Ground



Fig. 5 Open aperture Z-scan plotting for 2, 3 and 4 complexes.

state calculations were carried out with DFT.<sup>26</sup> The B3LYP functional<sup>27–29</sup> was used for optimizations and CAM-B3LYP (includes long-range-correction terms)<sup>30</sup> was used for obtaining UV-vis spectra in combination with the 6-31G(d,p) and with LANL2DZ basis sets<sup>31</sup> (for metals). The optimized structures were characterized as true minima without any imaginary frequencies. The first 140 singlet excited states of each system were considered in the TD-DFT calculations. Molecular orbital energies and UV-vis spectra were obtained using the optimized ground state geometries. Solvent effects in the ground state were studied using the polarizable continuum model (PCM).<sup>32,33</sup> The method in ref. 34 was used to calculate the nonlinear optical properties of the studied molecules.

## 3. Results and discussion

#### 3.1. Synthesis and characterization

The synthesis of the starting compound, 4,4'-(((2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diyl)bis(2-methylpropane-2,1-diyl)) bis(oxy))diphthalonitrile (1), was confirmed by the appearance of a typical nitrile band at 2230 cm<sup>-1</sup>, and a new absorption band at 1252 cm<sup>-1</sup> corresponding to the Ar–O–Ar bond in its IR spectrum. In addition, the reaction of bisphthalonitrile compound 1 leading to the formation of BTMPc complexes 2–4 was confirmed by the disappearance of the obvious nitrile band at 2230 cm<sup>-1</sup>, in their IR spectra. Moreover, the IR spectra of the BTMPcs indicated the close wavenumber values like 3075 cm<sup>-1</sup>, 3073 cm<sup>-1</sup> and 3076 cm<sup>-1</sup> (arom C–H), 2926–2849 cm<sup>-1</sup>, 2914–2849 cm<sup>-1</sup> and 2924–2853 cm<sup>-1</sup> (aliph C–H), 1606–1486 cm<sup>-1</sup>, 1610–1468 cm<sup>-1</sup>, and 1611–1466 cm<sup>-1</sup> (C==C), and 1227 cm<sup>-1</sup>, 1233 cm<sup>-1</sup>, and 1233 cm<sup>-1</sup> (C–O–C) for 2, 3 and 4 respectively.

The <sup>1</sup>H-NMR spectrum of bisphthalonitrile derivative **1** of the SPG starting compound (in CDCl<sub>3</sub>) gave the satisfactory results in the characterization of its proposed structure as esti-

mated. SPG is a highly symmetrical molecule but it should be chiral due to the presence of a chiral axis leading to a similar behaviour to that of its bisphthalonitrile derivative **1**.<sup>35</sup>

H1 shows aliphatic methyl (-CH<sub>3</sub>) protons as a doublet at 1.05 ppm. H2, H3, H4 and H7 indicated the aliphatic methylene (-CH<sub>2</sub>-) protons in the 2,4,8,10-tetraoxaspiro[5.5]undecane part of compound **1** as doublets at 3.33 ppm 3.50 ppm and 3.57 ppm and 4.48 ppm, respectively. In addition, H5 indicates methylene (-CH<sub>2</sub>-) protons adjacent to di-methyl substituted carbon and the oxygen atom bridged to the phthalonitrile moiety as double doublets at 3.83 ppm and 3.87 ppm in order. H6 shows aliphatic methine protons at 4.36 ppm as a singlet signal.

As in the aromatic region, H8, H9 and H10 yielded a double doublet at 7.17 ppm, a doublet band having a splitting of 2.65 Hz with *meta*-coupling at 7.26 and another doublet at 7.68 ppm respectively (Fig. 1).

On the other hand, due to the very low and broad signals, a satisfactory spectrum of the BTZnPc complex could not be obtained, because of its low solubility in any solvents. Therefore, it was difficult to characterize it with <sup>1</sup>H-NMR.

The <sup>1</sup>H–<sup>1</sup>H COSY spectrum of bisnitrile compound **1** confirmed that its synthesis and purification were successfully achieved. The data on the protons that are coupling with each other are acquired by studying the peaks in the <sup>1</sup>H–<sup>1</sup>H COSY NMR. From the 2D NMR we have identified two types of erythritol methylene protons connected to the central carbon atom. The spots marked with **A** and **B** indicate the interactions between the inequivalent (H7R:H3S)–(H7S:H3R) (3.33 ppm and 3.57 ppm) and (H2S:H4R)–(H2R:H4S) (3.50 ppm and 4.48 ppm) methylene protons of the erythritol moiety. Besides, the spot defined as **C** shows H8–H10 (7.17 ppm and 7.68 ppm) coupling in the aromatic nitrile moiety (Fig. 2).

Furthermore, the UV-vis spectra of all complexes 2, 3 and 4 displayed characteristic absorptions in the Q band region at 683 nm 670 nm and 672 nm in DMF, respectively. Furthermore, complexes 2, 3 and 4 exhibited satellite bands at 647 nm, 630 nm, and 632 nm, respectively, in turn. These BTMPcs also showed Soret (B) bands at about 353 nm 330 nm and 331 nm for 2, 3 and 4 respectively (Fig. 3). Due to the broadening of the Q band and more intensive soret band 3 and 4 also show aggregation.

The MALDI-TOF-MS spectra of the BTZnPc 2, BTCoPc 3 and BTCuPc 4 complexes were obtained and are given in Fig. 4. These complexes were ionized under MALDI-TOF-MS conditions in protonated ion forms. For all complex forms, the experimental and theoretical isotopic mass distributions were compared in each MALDI-TOF-MS spectrum as an inset spectrum. All complexes showed almost identical isotopic mass distributions with the theoretical isotopic mass distributions. In all the MALDI-TOF-MS spectra of the complexes, some fragment ions were observed because of the high laser energy used to obtain intense molecular ion signals. All highly intense fragment signals were checked and it was found that these fragment masses correlated with some fragmentation resulting from the complexes. All the information supported that the complexes were synthesized correctly in the desired forms.

#### 3.2. Nonlinear optical properties

The nonlinear optical properties of the phthalocyanines have recently attracted remarkable attention in photonic technologies due to their wide reverse saturable absorption, rapid response times and ease of chemical processing.<sup>36,37</sup>

Open aperture (OA) Z-scan experiments are performed to evaluate the nonlinear absorption coefficient. In the open aperture Z-scan method, there is no aperture in front of the detector and the measurements are implemented *via* translating the material in the positive and negative directions with respect to the focal point. The transmittance data show a peak or a valley at the zero point of the *z*-axis which corresponds to the focus of the beam. The peak indicates a negative absorption coefficient, while the valley gives a positive absorption coefficient.

All the chemicals are prepared at  $4.25 \times 10^{-4}$  M concentration in DMSO and then diluted into two other concentration values. The absorbance value of each complex is measured at 532 nm with a BioSpa 8 automated incubator. Absorption coefficients are derived and used in NLO calculations.

The open aperture plotting of the 2, 3 and 4 complexes at the initial concentration is given in Fig. 5. The input power was kept at  $3.0 \times 10^6$  W cm<sup>-2</sup> value for each complex to compare.

The nonlinear absorption coefficient is evaluated by fitting the data using the equation below,

$$T(z) = \frac{1}{\sqrt{\pi}q_0(z)} \int_{-\infty}^{\infty} \ln \left[ 1 + \left( \frac{\beta I_0 L_{\text{eff}}}{1 + \frac{z^2}{z_0^2}} \right) e^{-\tau^2} \right] d\tau \qquad (1)$$
$$L_{\text{eff}} = \frac{1 - e^{-\alpha L}}{\alpha} \qquad (2)$$

where,  $L_{\text{eff}}$  is the effective sample length,  $I_0$  is the peak irradiance at focus,  $\alpha$  is the linear absorption coefficient, and  $\beta$  is the nonlinear absorption coefficient which is an important parameter to confirm the material's acceptability for optical limiting. z and  $z_0$  are the axial positions of the sample concerning the central position for the focus and the Rayleigh length, respectively. Rayleigh length,  $z_0$ , is put forward as the space along the propagation direction of a beam from the focal waist to where the beam cross-section folded two times. The imaginary component of the third-order susceptibility known as  $\text{Im}(\chi^{(3)})$  is related to the nonlinear absorption per mole. The materials have the largest  $\text{Im}(\chi^{(3)})$  value which relies on the highest  $\beta$  value due to the values varying linearly with  $\beta$ which is given by the following equation.<sup>38</sup>

$$Im(\chi^{(3)})(esu) = 10^{-2} \frac{\varepsilon_0 n^2 c^2 \lambda \beta(cm W^{-1})}{4\pi^2}$$
(3)

where *n*, *c*,  $\epsilon_0$  and  $\lambda$  are known as the linear refractive index, the speed of light, the dielectric permittivity of vacuum and the wavelength of the excitation light, respectively.

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 Table 1
 Calculated NLO parameters of all Pc derivatives for 2, 3 and 4 complexes

Pcs. complexes	Concentration $(\times 10^{-4} \text{ M})$	$ \begin{array}{c} \beta \left( \times 10^{-7} \\ \mathrm{cm} \mathrm{W}^{-1} \right) \end{array} $	$\operatorname{Im}(\chi^{(3)})$ (esu)	$\alpha_0$ (1/cm)
BTZnPc (2)	4.25	0.88	$0.21 \times 10^{-12}$	2.23
	2.13	0.41	$0.09  imes 10^{-12}$	1.14
	1.06	0.14	$0.03 \times 10^{-12}$	0.63
BTCoPc (3)	4.27	5.08	$0.12 \times 10^{-11}$	3.39
	2.14	4.92	$0.11\times10^{-11}$	2.05
	1.06	3.49	$0.08\times10^{-11}$	1.19
BTCuPc (4)	4.25	13.26	$0.31 \times 10^{-11}$	3.64
	2.13	5.85	$0.14 \times 10^{-11}$	1.15
	1.06	4.16	$0.10  imes 10^{-11}$	0.58
	1.06	4.16	$0.10 \times 10^{-11}$	0.5

All the data obtained using the open-aperture Z-scan technique were fitted using the method of least-squares regression with eqn (1)–(3). The free parameters  $\beta$  and Im( $\chi^{(3)}$ ) were calculated for the studied concentration and are given in Table 1.

The linear absorbance values of each complex are given in Table 1 and the Cu complex shows the maximum nonlinear absorption coefficient and imaginary part of the third-order susceptibility. Therefore, as expected, the highest nonlinear response is achieved for the complex BTCuPc in Fig. 6. Complex 4 also shows the highest nonlinear absorption (NLA) coefficient,  $\beta$ . The highest beta values belong to BTCuPc, and this result also indicates that the intermolecular interaction effects play an important role in the nonlinear optical (NLO) properties of BTCuPc.<sup>39</sup>

The sequential plots for complexes 2, 3 and 4 indicate the concentration dependent nonlinear response. As the intermolecular interaction states increase due to the concentration, the nonlinear response of all the complexes results in accompanying deep valleys on the transmission curves. The ideal optical limiter shows the linear transmittance at low powers, and it exhibits slightly opaque transmittance at high incident intensities.

So the investigation of the optical limiter properties of the novel nonlinear optical materials is vital to protect human eyes and sensitive solid state optical sensors from intense laser beams.<sup>40,41</sup> These properties of the materials are convenient for potential applications such as laser power regulation, and stabilization or restoration of signal levels in optical data transmission or logic systems.<sup>42,43</sup>

In organometallic complexes OPL performance is generally achieved using several optically nonlinear processes such as two-photon absorption (TPA) in combination with reverse saturation absorption (RSA).<sup>44,45</sup> TPA depends on intensity instead of fluence, so the mechanism does not successfully achieve an efficient laser protection for nanosecond pulses or longer. To alter this, a combination with RSA has high potential for the protection against longer pulses. The Z-scan profiles of all samples show typical RSA signatures, and the measurements indicate that an induced positive nonlinear absorption (NLA) of the laser light occurs due to the intensity-dependent absorption of the incident light.



Fig. 6 Nonlinear response of 2, 3 and 4 complexes at various concentrations.



Fig. 7 Nonlinear optical response of 2, 3 and 4 complexes due to excitation pulse energy.

The spectra in Fig. 7 demonstrate the nonlinear optical response of all the complexes due to the adjusted excitation pulse energy at 532 nm. All the complexes show a decrease in the excitation power at the focal point of the lens. These valleys clearly show an optical limiting behavior while the input power increases at around the focal point. RSA is the main mechanism of the

reduced transmittance curves for a successful optical limiting process. The highest decrease in the transmittance is observed for complex 4 (BTCuPc) which is in agreement with Fig. 5 and Table 1. This provides also the highest nonlinear optical absorbance coefficients for complex 4. The nonlinear optical response even at very low intensity pulses is still observable.

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Table 2 shows the nonlinear absorbance coefficient variation due to the adjusted excitation power values. Excitation power is the measurement of the energy values at the focal point of the lenses and increasing excitation powers indicate much higher nonlinear absorbance coefficients. In all, complex 4 results in the highest  $\beta$  values and Fig. 7 shows the variation of the nonlinear optical response valleys for each complex at adjusted excitation powers at the initial concentration.

Fig. 8 shows the combination of the second order-nonlinear absorption coefficient due to the incoming laser power for each complex. As it is also presented in Table 2 the maximum nonlinear response has been achieved for complex 4. This high NLO response can be achieved due to the aggregation in

 Table 2
 Nonlinear absorbance coefficients due to excitation power for

 2, 3 and 4 complexes

Pcs. complexes	Excitation power $(\times 10^6 \text{ W cm}^{-2})$	$eta \left(  imes 10^{-7} \ { m cm W^{-1}}  ight)$	$\operatorname{Im}(\chi^{(3)})$ (esu)
BTZnPc (2)	7.00	0.58	$0.14 \times 10^{-12}$
	3.04	0.77	$0.18 \times 10^{-12}$
	2.23	0.95	$0.22 \times 10^{-12}$
BTCoPc (3)	6.81	3.25	$0.76 \times 10^{-12}$
	3.38	1.80	$0.42 \times 10^{-12}$
	2.69	1.17	$0.27 \times 10^{-12}$
	1.83	1.62	$0.38 \times 10^{-12}$
	1.53	1.36	$0.32 \times 10^{-12}$
BTCuPc (4)	3.69	12.16	$0.28 \times 10^{-11}$
	2.93	10.58	$0.25 \times 10^{-11}$
	2.78	8.32	$0.19 \times 10^{-11}$
	2.50	8.03	$0.19 \times 10^{-11}$
	1.69	7.79	$0.18 \times 10^{-11}$
	1.41	6.04	$0.14 \times 10^{-11}$
	1.06	4.71	$0.11 \times 10^{-11}$
	0.96	2.54	$0.06 \times 10^{-11}$



Fig. 8 Nonlinear absorption coefficients of 2, 3 and 4 complexes due to excitation pulse energy at the initial concentrations of each complex.

the Cu complex and it may cause an increase in the intermolecular interactions which helps in the fast decaying of the upper triplet states. The broadening of the Q-bands of complex 4 in Fig. 4 indicates the molecular aggregation in the solutions of the BTCuPc complex. Furthermore, Table 2 clearly indicates that the Cu complex has an approximately ten times higher component of the third-order susceptibility known as  $Im(\chi^{(3)})$  compared to Co and Zn. This result may depend on the intermolecular interaction effect on the NLO properties of copper phthalocyanine.<sup>39</sup> The nonlinear optical responses of the freshly synthesized novel 4,4'-(((2,4,8,10-tetraoxaspiro [5.5]undecane-3,9-diyl)bis(2-methylpropane-2,1-diyl))bis(oxy)) bridged ball-type metallophthalocyanines in this study show that the copper complexes have distinctly high nonlinear optical response and this is a clear indicator of this novel ball type copper phthalocyanine which may be a good candidate in the applications of optical limiters.

#### 3.3. Computational results

The optimized structures of 2, 3 and 4 in the ground-state in DMF ( $\varepsilon = 37.22$ ) are given in Fig. 9 at the B3LYP/6-31G(d,p) level with the LANL2DZ basis set on the metals. Fig. S1† also shows the molecular structures of the investigated molecules in DMF in different views.

Some of the selected parameters of the molecules calculated with the B3LYP functional including dipole moments ( $\mu$ , Debye) and the sum of electronic energies with zero-point energy corrections ( $E_{elec}$  + ZPE, Hartree) in DMF are given in Table 3. The dipole moments of the molecules are almost similar. BTCoPc 3 and BTCuPc 4 maintain their square planar (SP) geometries; on the other hand, BTZnPc 2 deviates by 15° from the square planar geometry. Deviation from the molecular planarity and the distortion of the SP geometry around the zinc atom increase the intramolecular metal-metal (M-M) distance (11.78 Å). The average vertical distance of the molecules is approximately 10 Å and the average horizontal distance is approximately 20 Å. However, the parallel Pc rings do not display a perfect double decker geometry as there are shifts between the metal centers. These shifts are measured as 14.70°, 10.53° and 8.28° for 2, 3 and 4, respectively. These shifts may be attributed to the presence of long bridging ligands between the Pcs as single bonds of these ligands provide flexibility for the molecule.

B3LYP/6-31G(d,p)/LANL2DZ and CAM-B3LYP/6-31G(d,p)/ LANL2DZ levels were used in TD-DFT calculations to obtain



**Fig. 9** Optimized geometries of **2**, **3** and **4** in DMF (hydrogen atoms are excluded for simplicity for a clear presentation).

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**Table 3** Dipole moments ( $\eta$ ), sum of total electronic energies and zero point energies ( $E_{elec}$  + ZPE), and selected interatomic distances and angles of the investigated compounds in DMF calculated at the B3LYP/ 6-31G(d,p)/LANL2DZ levels

	2	3	4
μ (D)	6.80	7.46	6.88
$E_{\rm elec}$ + ZPE (Hartree)	-7612.8010	-7771.7171	-7873.8109
Distances (Å)			
M-M <sup>a</sup>	11.78	10.45	10.54
Vertical <sup>b</sup>	10.74	10.06	10.49
Horizontal <sup>c</sup>	21.72	21.12	21.86
Angles			
(Pc1–Pc2)° shift	14.70	10.53	8.28
N1-M-N3	164.31	179.60	179.64
N2-M-N4	164.40	179.68	179.99
N5-M-N7	164.73	178.94	179.13
N6-M-N8	164.06	178.62	178.62

<sup>*a*</sup> M: metal. <sup>*b*</sup> Vertical distance between the metal in Pc1 and corresponding atom in Pc2. <sup>*c*</sup> Horizontal distance between the symmetrical ligands.

the absorption wavelengths and excitation energies for the first 140 singlet excited states (from  $S_0$  to S140) for 2. The CAM-B3LYP values are in better agreement with the experimental results in DMF (Fig. S2†); thus, the following discussion is based on the CAM-B3LYP/6-31G(d,p) results unless otherwise stated.

Also, the TD-DFT calculations of 4 (CuPc) with CAM-B3LYP and LC-BLYP functionals were compared with the experimental UV-vis results (first 140 singlet states) (Fig. S3†). It has been observed that CAM-B3LYP also gives results similar to the experimental results at longer wavelengths for 4. Considering these results and the literature indicating that CAM-B3LYP gives better results in TD-DFT calculations for similar systems,<sup>46,47</sup> the UV-vis absorptions of all studied molecules were measured using the CAM-B3LYP functional.

Fig. 10 shows the calculated UV-vis absorption spectra of compounds 2, 3 and 4. The characteristic Q and B bands are significant, but their absorption intensity is different from each other. Compound BTZnPc 2 displays  $\pi$ - $\pi$ \* transitions (Table S1 and Fig. S4†), whereas compounds 3 and 4 display transitions mostly including metals (Tables S2, S3, Fig. S5 and S6†). Since Co and Cu have an odd number of electrons (Co<sup>II</sup>, d<sup>7</sup> and Cu<sup>II</sup>, d<sup>9</sup> configurations), this may cause low intensity d–d transitions and may ease their contributions to other electronic transitions (MLCT and LMCT).

Q-band transitions to  $S_1$ ,  $S_2$ ,  $S_3$ ,  $S_4$  (between 705.5 nm and 694.3 nm) display the local excitation of Pc1 (LE Pc1) and Pc2 (LE Pc2) in compound 2. The electrons move from O to Pc (LCT: ligand charge transfer) at lower wavelengths (between 358.2 nm and 306.4 nm). B-bands with high oscillator strengths are observed between 334.4 and 318.5 nm in compound 2. Both Q and B bands are in good agreement with the experimental results. Metal-to-ligand charge transfer was observed at 301.1 nm with very low oscillator strength. In addition, charge transfers between the Pcs (Pc1 and Pc2) were observed around 335 nm.





Fig. 10 The UV-vis absorption spectra of 2, 3 and 4 (with oscillator strength values) in DMF calculated at the CAM-B3LYP/6-31G(d,p) and LANL2DZ (for metals) level.

The calculations showed that compounds 3 and 4 have transitions in the near-IR region. Thus, discussion in the UV region started at the S0  $\rightarrow$  S13 transition (773 nm) for 3 and at the S0  $\rightarrow$  S8 transition (713 nm) for 4. Both have  $\pi \rightarrow \pi^*$  character (LE Pc) and the d–d transition (local excitation Co and Cu) between HOMO–4/LUMO+1 and HOMO–2/LUMO+1, respectively. The S0  $\rightarrow$  S18 transition (607 nm) shows also local excitation of the phthalocyanine ring (LE,  $\pi \rightarrow \pi^*$  character) with high oscillator strength. Q-bands are observed between 772 nm and 603 nm for compound 3. Metal-to-ligand charge transfer (MLCT: charge transfer from Co to Pc) was first observed at 609 nm between HOMO–6 (d<sub>z</sub><sup>2</sup>) and LUMO+2. The

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d-d transition was also observed at the same wavelength. Similar observations were made at 602.6 nm and 594.1 nm.

The ligand-to-metal charge transfer (LMCT: charge transfer from Pc to Co) transition was observed at 605.3 nm with LE Pc. In addition, both LMCT and local excitation in the Pc were observed between 396.0 nm and 326.8 nm. Apart from metal ligand interactions, charge transfers from the bridge to Pc take place (LCT: charge transfer from O to Pc). These transitions are also observed with low oscillator strength between 519.2 nm and 421.2 nm in addition to the ones observed at 325.2 nm and 310.8 nm for compound **3**.

Compounds 3 and 4 have similar UV-vis absorption characteristics. In compound 4, the d orbitals contributed to all electronic transitions. There are intense Q-bands at 654.2 nm and 648.6 nm. These transitions display LMCT character from Pc to Cu. Metal-to-ligand charge transfers (MLCT) with a low oscillator strength between the HOMO and LUMO+10 were observed at 452.0 nm and 449.5 nm. In addition, MLCTs were observed at 418.6 nm, 396.2 nm, 331.4 nm, 321.3 nm, and 305.9 nm. In the investigated UV and vis regions, a charge transfer from the ligand to Pc (LCT) was observed. There are B-bands between 331 nm and 308 nm.

The frontier molecular orbitals and energy gaps of 2, 3 and 4 in DMF are shown in Fig. S7.<sup>†</sup> As seen from the figure, the HOMO and LUMO are localized on different parts of the molecules with changing the metal on Pc. While the HOMOs are localized mostly on the  $\pi$ -bonding orbitals of Pc for 2 and 3, the LUMOs are localized on the  $\pi$ -antibonding orbitals of Pc in compound 2, at the Pc and Co centres in compound 3. The HOMO and LUMO are localized on the d orbitals of Cu and bonding electrons of Pc for compound 4 (Fig. S7<sup>†</sup>). The value of energy separation between the HOMO and LUMO is 3.65 eV, 1.24 eV and 0.68 eV for 2, 3 and 4 respectively. A low energy gap between the HOMO and LUMO facilitates the charge transfer and thus makes the material NLO active (Fig. S8<sup>†</sup>).

DFT has been widely used as an effective method to compute the properties of the NLO materials. According to previous studies, the CAM-B3LYP method is more reliable in the polarizability calculations of large molecular systems.<sup>48–50</sup> The electric dipole moment,  $\mu$ , polarizability,  $\alpha$ , and first-order hyperpolarizability,  $\beta_0$  and their components are calculated using CAM-B3LYP/6-31G(d,p)/LANL2DZ basis sets in the gas phase and are listed in Table S4.<sup>†</sup> The calculated dipole moments  $\mu$  of the investigated compounds were found to be similar (3.60, 3.34 and 4.24 Debye for 2, 3 and 4, respectively). The value of  $\beta_{\rm tot}$  is 8.92 × 10<sup>-30</sup> esu, 117.06 × 10<sup>-30</sup> esu and  $409.81 \times 10^{-30}$  esu for 2, 3 and 4, respectively. The larger value of Cu among all can be attributed to the decrease in the HOMO-LUMO difference with changing the metal. These values are nearly 19, 254 and 891 times larger than that of urea at the same level  $(0.46 \times 10^{-30} \text{ esu})$  for 2, 3 and 4, respectively. The BTCuPc complex is a conjugated  $\pi$ -electron system with a two-dimensional conjugation decreasing the HOMO-LUMO gap. This enhances the intramolecular charge transfer which gives rise to nonlinear optical properties with the third harmonic generation.<sup>51</sup> Furthermore, the good optical limiting

efficiency originates primarily from reverse saturable absorption, which is entirely due to the first excited triplet state.<sup>52</sup> As a consequence, BTCuPc, among others, shows the best optical limiting performance. These results indicate that the investigated compounds are potentially good NLO material candidates. The large hyperpolarizability value is associated with the intramolecular charge transfer, resulting from the electron cloud movement through the  $\pi$  conjugated groups and metal centers.<sup>53</sup>

## 4. Conclusions

Novel SUBO bridged ball-type metallophthalocyanines were accomplished and their structures were confirmed using IR, <sup>1</sup>H-NMR, <sup>1</sup>H-<sup>1</sup>H-COSY-NMR, UV-vis and MALDI TOF mass spectroscopic methods.

The nonlinear optical properties of the Pc derivatives with various concentrations have been studied and nonlinear optical parameters were determined. All the data obtained using the open-aperture Z-scan technique were fitted using the method of least-squares regression. The results show that the highest nonlinear absorption coefficient and imaginary component of the third-order susceptibility are achieved for complex BTCuPc 4 due to the intermolecular interaction effects. It can be concluded that 4 is much more attractive than 2 and 3 due to its nonlinear optical properties and the computational results are also in agreement with the experimental results.

## Conflicts of interest

There are no conflicts to declare.

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