JOURNAL OF CHEMICAL RESEARCH 2012 NOVEMBER, 657–659 **RESEARCH PAPER** 657

Synthesis and characterisation of new metallophthalocyanines containing four 12-membered diazadithia-macrocyclic moieties

Elif Çelenk Kaya[a]*, Halit Kantekin[b], Afşin Ahmet Kaya[a], Asuman Dakoğlu[b], Sümeyra Öksüz[b] and Hanife Şişik[b]

[a] *Gümüşhane Vocational and Training School, Gümüşhane University, 29100 Gümüşhane, Turkey*

[b] *Department of Chemistry, Faculty of Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey*

Tetrasubstituted zinc, cobalt, nickel, copper and lead phthalocyanines bearing four 12-membered diazadithia macrocyclic moieties on peripheral positions have been synthesised by cyclotetramerisation reaction of 1,10-ditosyl-1,2,3,5,6,8,9,10-octahydrobenzo[h][1,4,7,10]dithiadiazacyclododecine-12,13-dicarbonitrile and corresponding anhydrous metal salts under microwave irradiation. The thermal stabilities of the phthalocyanine compounds have determined by thermogravimetric analysis.

Keywords: phthalocyanine, metallophthalocyanine, macrocyclic compound, mixed-donor macrocyclic, microwave irradiation

Metal porphyrin complexes [MP(-2)] play a vital role in biological processes such as photosynthesis and respiration. These complexes have a unique chemistry with several existing and potential industrial applications. The most commercially important group of the porphyrin class of molecules is the phthalocyanines, known systematically as tetrabenzo [5,10,15,20]tetraazaporphyrins.[1] Metal phthalocyanines and their peripherally substituted derivatives have technological and commercial applications as dyes and printing inks. In recent decades, there has been renewed interest in the use of phthalocyanine complexes in high technology fields including use in semiconductor devices,[2] photovoltaic and solar cells,[3,4] electrophotography,[5] rectifying devices,[6] molecular electronics,[7] Langmuir–Blodgett films,[8,9] electrochromism in display devices,[10] low dimensional metals,[11] gas sensors,[12,13] liquid crystals,[14] and nonlinear optics,[15,9] and as photosensitisers[16] and electro catalytic agents.[13,17]

In photodynamic therapy (PDT), singlet oxygen is generated using photosensitiser and dioxygen *via* several energy transfer steps.[18,19] Phthalocyanines are better photosensitisers for PDT than others, such as porphyrins and naphthalocyanines. They exhibit effective tissue penetration because of their chemical stability, photodynamic activity, and proper light absorption region. Singlet oxygen has been to cause tumor necrosis[20,21] and also induce several biological reactions.[22,23] Nevertheless, the existence of singlet oxygen seems to be indefinite in the solution. The presence of singlet oxygen is essential in photodynamic therapy.

Microwave (MW) irradiation can accelerate a great number of chemical processes, and, in particular, the reaction time and energy input are reduced compared with reactions that are run for a long time at high temperatures under conventional conditions.[24]

We have previously descibired the synthesis and characterisation of some polymeric metal-free and metalophthalocyanines by microwave irradiation.[25] We now describe the synthesis, spectral and thermal characterisation of novel metallophthalocyanines bearing macrocyclic N_2S_2 donor groups on peripheral positions.

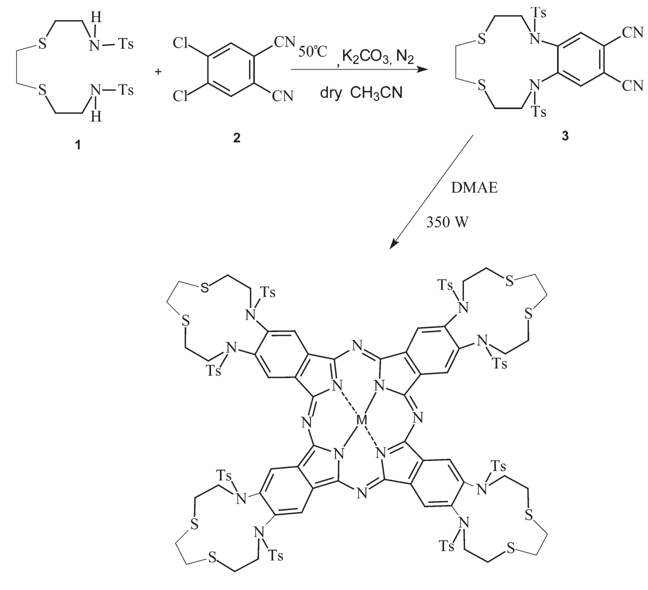
Results and discussion

Compound **3** was synthesised by the reaction of N,N′-(2,2′-(ethane-1,2-diylbis(sulfanediyl))bis(ethane-2,1-diyl))bis (4-methyl benzenesulfonamide) **1** with 1,2-dichloro-4,5-dicyanobenzene **2** in dry acetonitrile containing finely ground anhydrous K_2CO_3 as a template agent at reflux temperature in a Schlenk system under an N_2 atmosphere (Scheme 1).

Dicyano compound **3** was obtained in 54% yield after being purified by column chromatography on silica gel using (30% hexane/ethyl acetate) as eluent. Analytical and spectroscopic data of **3** clearly confirm the success of the cyclisation reaction. Comparison of their IR spectral data clearly indicate the formation of compound **3** by the disappearence of the NH band of compound **1** at 3285 cm^{-1}, and the appearance of a new absorption at 2233 cm^{-1} ($C\equiv N$). In the ^1H NMR spectrum of **3**, the signals belonging to NH protons (δ = 5.33 ppm) in the precursor compound **3** were absent after the macrocyclisation reaction.

The ^{13}C NMR spectrum of **3** shows the presence of nitrile carbon atoms at δ = 115.48 ppm which indicates the completion of conversion of **1** to **3**. FAB mass spectrum and elemental analysis also confirm the formation of compound **3**.

Metallophthalocyanines were obtained from dicyano derivative **3** and the corresponding anhydrous metal salts $Zn(CH_3COO)_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $PbCl_2$ respectively, by microwave irradiation in 2-(dimethylamino)ethanol in the range of 10 min. In the IR spectra of metallophthalocyanines, the disappearance of the strong $C\equiv N$ stretching vibration of **3** is an evidence for the formation of metallophthalocyanines.



Scheme 1 The synthesis of the metallophthalocyanines **4, 5, 6, 7** and **8**.

Compd	**4**	**5**	**6**	**7**	**8**
M	Zn	Co	Ni	Cu	Pb

---

* Correspondent. E-mail: elifcelenk1629@hotmail.com

In the mass spectrum of compounds **4**, **5**, **6**, **7** and **8**, the presence of molecular ion peaks at *m/z*= 2516[M]$^+$, 2549[M+K]$^+$, 2532[M+Na]$^+$, 2515[M+1]$^+$, 2659 [M+1]$^+$ respectively, confirmed the proposed structures. The elemental analyses also confirm the proposed formulations.

UV-Vis spectra of the phthalocyanine complexes exhibit characteristic Q and B bands. The Q-band in the visible region at 600–750 nm (Q-band) is attributed to the π–π* transition from HOMO to the LUMO of the Pc(-2) ring, and the B-band in the UV region at 300–400 nm (B-band) arises from the deeper π–π* transitions.[26]

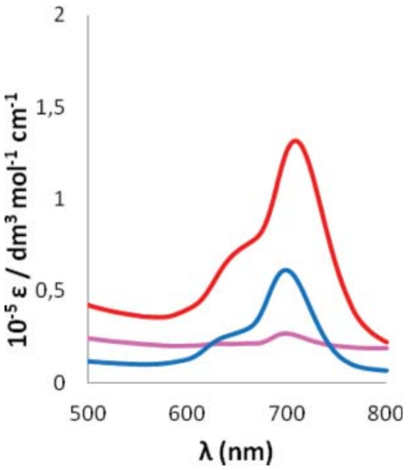


Fig. 1 UV-Vis spectra of ZnPc (**4**) in chloroform (—), THF (—), pyridine (—).

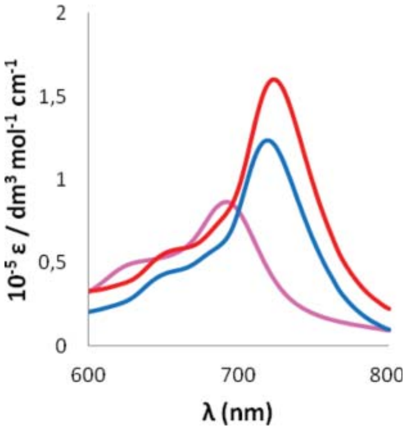


Fig. 2 UV-Vis spectra of CoPc (**5**) in chloroform (—), THF (—), pyridine (—).

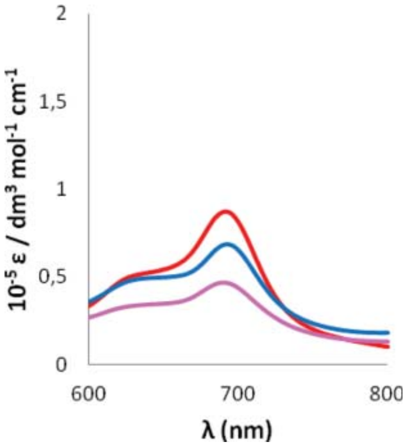


Fig. 3 UV-Vis spectra of NiPc (**6**) in chloroform (—), THF (—), pyridine (—).

Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes. It is dependent on the concentration, nature of the solvent, nature of the substituents, complexed metal ions and temperature.[27] In this study, the aggregation behaviour of the phthalocyanine complexes (ZnPc, CoPc and NiPc) were investigated in different solvents (chloroform, THF and pyridine), (see Figs 1, 2 and 3). It has been observed that aggregation increases and the intensity of absorption of the Q band decreases along with the increase of the solvent polarity.

The thermal behaviour of the metallophthalocyanines were investigated by TG/DTA. Although the thermal stabilities of phthalocyanines is well known, these phthalocyanine compounds are not stable above 208 °C. The initial and main decomposition temperatures are given in Table 1. The initial decomposition temperature decreased in the order: **8** > **6** > **7** > **5**>.

Conclusion

We have described the synthesis, spectral and thermal characterisation of novel metallophthalocyanines bearing macrocyclic N_2S_2 donor groups on peripheral positions. For this, N,N′-(2,2′-(ethane-1,2-diylbis(sulfanediyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) **1** was reacted with 1,2-dichloro-4,5-dicyanobenzene **2** in dry acetonitrile containing finely ground anhydrous K_2CO_3 as a template agent to give compound **3**. The metallophthalocyanines **4**, **5**, **6**, **7** and **8** were obtained from dicyano derivative **3** and corresponding anhydrous metal salts $Zn(CH_3COO)_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $PbCl_2$ respectively, by microwave irradiation in 2-(dimethylamino)ethanol for at 175 °C, 350 W for 10 min. The thermal stabilities of the metallophthalocyanine compounds were determined by thermogravimetric analysis.

The new macrocyclic compound **3** bearing soft sulfur donor atoms, moderate soft nitrogen donor atoms and the new metallo phthalocyanines **4**, **5**, **6**, **7** and **8** containing macrocyclic N_2S_2 donor groups on peripheral positions might be used in selective extraction of alkali, alkali earth and transition metal ions. This field will form an important area of future study.

Experimental

N,N′-(2,2′-(ethane-1,2-diylbis(sulfanediyl))bis(ethane-2,1-diyl))bis (4-methyl benzenesulfonamide) **1** and 1,2-dichloro-4,5-dicyanobenzene **2**[28,29] were prepared according to the reported procedures. All reactions were carried out under a dry N_2 atmosphere using standard Schlenk techniques. The IR spectra were recorded on a Perkin-Elmer 1600 FTIR Spectrophotometer, using potassium bromide pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$, and chemical shifts are reported (δ) relative to Me_4Si as internal standard. Mass spectra were measured on a Varian 711 and VG Zapspec spectrometers. Elemental analyses were determined by a LECO Elemental Analyser (CHNS O932) and Unicam 929 AA spectrophotometer. UV-Vis absorpion spectra were measured by a Unicam UV-Vis spectrometer. Melting points were measured on an electrothermal apparatus. A Seiko II Exstar 6000 thermal analyser was used to record DTA curves under N_2 with a heating rate of 20 °C min^{-1} in the temperature range 30–900 °C using platinum crucibles. A domestic oven (Arçelik MD 823, 350 W) was used for all the synthesis of metallo phthalocyanines.

Table 1 Thermal properties of the metallo phthalocyanines

Compd	M	İnitial decomposition Temperature/°C	Main decomposition Temperature/°C
4	Zn	219	274
5	Co	208	268
6	Ni	276	357
7	Cu	268	303
8	Pb	286	318

Table 2 Some analytical data and physical properties of the new compounds

Compd	Empirical formula	Colour	Formula wt	M.p. /°C	Yield /%
3	$C_{28}H_{28}N_4O_4S_4$	Yellow	612	182–184	54
4	$C_{112}H_{112}N_{16}O_{16}S_{16}Zn$	Dark green	2516	>300	31
5	$C_{112}H_{112}N_{16}O_{16}S_{16}Co$	Dark green	2510	>300	33
6	$C_{112}H_{112}N_{16}O_{16}S_{16}Ni$	Dark green	2509	>300	26
7	$C_{112}H_{112}N_{16}O_{16}S_{16}Cu$	Dark green	2514	>300	28
8	$C_{112}H_{112}N_{16}O_{16}S_{16}Pb$	Dark green	2658	>300	27

110-Ditosyl-1,2,3,5,6,8,9,10-octahydrobenzo[h][1,4,7,10 dithiadiazacyclodode cine-12,13-dicarbonitrile (**3**): N,N′-(2,2′-(ethane-1,2-diylbis(sulfanediyl))bis(ethane-2,1-diyl))bis(4-methylbenzenesulfonamide) (**1**)[28] (1.8g., 3.68 mmol) was dissolved in dry acetonitrile (60 mL), finely ground anhydrous K_2CO_3 (1.53 g, 11.06 mmol) was added and the mixture stirred for 2h. at 50 °C. A solution of 1,2-dichloro-4,5-dicyanobenzene (**2**)[29] (0.72g, 3.68 mmol) in dry acetonitrile (30 mL) was added dropwise over 3h. After stirring for 6 days at reflux temperature, the solvent was removed under reduced pressure, the residue mixed with water (50 mL) and then extracted with chloroform (3×50 mL). The organic layer was dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure to give an orange-coloured crude product. The product was purified by column chromatography with silica gel [hexane/ethyl acetate (3:2)]. Finally a yellow solid product (**3**) was obtained. Compound **3** was soluble in chloroform, dichloromethane and dimethyl formamide. Yield: 1.22g. (54%), m.p. 182–184 °C; δ_H (200 MHz, $CDCl_3$) 8.05 (s, ArH, 2H), 7.50 (d, *J* = 7.21 Hz, A part of AB system, Ar-Ts-H, 4H), 7.32 (d, *J* = 7.21 Hz, B part of AB system, Ar-Ts-H, 4H), 4.14 (t, *J* = 5.02 Hz, N–CH_2, 4H), 3.94(t, *J* = 3.91 Hz, S–CH_2, 4H), 2.88(t, *J* = 4.29 Hz, S–CH_2, 4H), 2.43 (s, CH_3, 6H); δ_C (100 MHz, $CDCl_3$) 145.7, 136.1, 131.4, 130.7, 130.3, 127.2, 115.4 (C≡N), 48.5 (N–CH_2), 44.9 (S–CH_2), 43.4 (S–CH_2), 21.9 (CH_3); ν_{max} (KBr/cm^{-1}) 3027 (ArH), 2956- 2923 (Aliph.-C–H), 2233 (C≡N), 1713, 1584, 1526, 1483, 1359, 1232, 1163, 1087, 814. Anal. Calcd for $C_{28}H_{28}N_4O_4S_4$: C, 54.88; H, 4.61; N, 9.14; S, 20.93. Found: C, 54.44; H, 4.56; N, 9.08; S, 19.82%. MS: *m/z* 613 [M^++1].

*General procedure for metallophthalocyanine derivates (**4–8**)*

A mixture of compound **3** (0.200 g, 0.327 mmol), anhydrous metal salts [$Zn(CH_3COOH)_2$ (0.015 g, 0.08 mmol), $CoCl_2$ (0.0107 g, 0.08 mmol), $NiCl_2$ (0.0107 g, 0.08 mmol), $CuCl_2$ (0.0107 g, 0.08 mmol) or $PbCl_2$ (0.0107 g, 0.08 mmol)] and 2-(dimethylamino)ethanol (2 mL) was irradiated in a microwave oven at 175 °C, 350 W for 10 min. After cooling to room temperature the reaction mixture was washed with hot EtOH–MeOH and dried *in vacuo*. The solid product was purified by column chromatography with silica gel [chloroform/methanol (10: 1) as eluents].

Zinc (II) phthalocyanine (**4**): Yield: 0.064g. (%31), m.p. > 300 °C; δ_H (200 MHz, $CDCl_3$) 7.73 (m, ArH, 8H), 7.56 (m, ArH, 32H), 4.10 (t, *J* = 6.63 Hz, N–CH_2, 16H), 2.43 (t, *J* = 5.74 Hz, S–CH_2, 16H), 2.02 (t, *J* = 6.13 Hz, S–CH_2, 16H), 1.70 (s, CH_3, 24H); ν_{max} (KBr/cm^{-1}) 3043 (ArH), 2918–2846 (Aliph.-C–H), 1596 (aromatic–C═C–), 1481, 1401, 1374, 1320, 1153, 1062, 932, 875, 744. UV-Vis ($CHCl_3$): λ_{max}/cm^{-1} 693(5.27), 653(5.03), 350(4.57), 242(5.25). Anal. Calcd for $C_{112}H_{112}N_{16}O_{16}S_{16}Zn$: C, 53.46; H, 4.49; N, 8.90; S, 20.38. Found: C, 53.54; H, 4.38; N, 8.62; S, 19.93%. MS: *m/z* 2516 [M^+].

Cobalt(II) phthalocyanine (**5**): Yield: 0.068g. (33%), m.p. > 300 °C; ν_{max} (KBr/cm^{-1}) 3060 (ArH), 2923–2851 (Aliph.-C–H), 1596 (aromatic–C═C–), 1414, 1345, 1159, 1088, 954, 812, 706. UV-Vis ($CHCl_3$): λ_{max}/cm^{-1} 698(4.96), 632(4.75), 317(5.08), 287(5.11). Anal. Calcd for $C_{112}H_{112}N_{16}O_{16}S_{16}Co$: C, 53.59; H, 4.49; N, 8.93; S, 20.44. Found: C, 53.66; H, 4.31; N, 8.43; S, 20.54%. MS: *m/z* 2549 [M^++K].

Nickel(II) phthalocyanine (**6**): Yield: 0.053g. (26%), m.p.: >300 °C; δ_H (200 MHz, $CDCl_3$) 7.83 (m, ArH, 8H), 7.38 (m, ArH, 32H), 4.42 (t, *J* = 6.51 Hz, N–CH_2, 16H), 2.56 (t, *J* = 5.23 Hz, S–CH_2, 16H), 2.43 (t, *J* = 6.02 Hz, S–CH_2, 16H), 1.59 (s, CH_3, 24H); ν_{max} (KBr/cm^{-1}) 3060 (ArH), 2928–2857 (Aliph.-C–H), 1596 (aromatic–C═C–), 1419, 1349, 1159, 1088, 960, 813, 668. UV-Vis ($CHCl_3$): λ_{max} / cm^{-1} 698(4.71), 632(4.57), 275(5.22). Anal. Calcd for $C_{112}H_{112}N_{16}O_{16}S_{16}Ni$: C, 53.61; H, 4.50; N, 8.93; S, 20.44. Found: C, 53.86; H, 4.46; N, 8.34; S, 20.17%. MS: *m/z* 2532 [M^++Na].

Copper (II) phthalocyanine (**7**): Yield: 0.057g. (28%), m.p. >300 °C; ν_{max} (KBr/cm^{-1}) 3071(ArH), 2919–2846 (Aliph.-C–H), 1591 (aromatic–C═C–), 1327, 1259, 1155, 1080, 809, 743. UV-Vis ($CHCl_3$): λ_{max} / cm^{-1} 707(4.59), 341(5.06), 278(5.26). Anal. Calcd for $C_{112}H_{112}N_{16}O_{16}S_{16}Cu$: C, 53.50; H, 4.49; N, 8.91, S, 20.40. Found: C, 53.27; H, 4.14; N, 8.52; S, 19.98%. MS: *m/z* 2515[M^++1].

Lead (II) phthalocyanine (**8**): Yield: 0.058g. (27%), m.p. >300 °C; δ_H (200 MHz, $CDCl_3$) 7.63 (m, ArH, 8H), 7.38 (m, ArH, 32H), 4.38 (t, *J* = 6.43 Hz, N–CH_2, 16H), 2.63 (t, *J* = 5.34 Hz, S–CH_2, 16H), 2.35 (t, *J* = 6.13 Hz, S–CH_2, 16H), 1.62 (s, CH_3, 24H); ν_{max} (KBr/cm^{-1}) 3065(ArH), 2921–2846 (Aliph.-C–H), 1593(aromatic–C═C–), 1404, 1371, 1156, 1085, 938, 809. UV-Vis ($CHCl_3$): λ_{max} / cm^{-1} 734(4.91), 662(4.49), 344(5.00), 278(5.24). Anal. Calcd for $C_{112}H_{112}N_{16}O_{16}S_{16}Pb$: C, 50.61; H, 4.25; N, 8.43, S, 19.30. Found: C, 50.35; H, 4.16; N, 8.50; S, 19.24%. MS: *m/z* 2659 [M^++1].

This work was supported by The Scientific Technological Research Council of Turkey (TÜBİTAK Project no: 107T429).

Received 12 August 2012; accepted 30 August 2012
Paper 1201459 doi: 10.3184/174751912X13472922835683

References

1 E.A. Lukyanets and V.N. Nemykin, *J. Porphyr. Phthalocya.*, 2010, **14**, 1–40.
2 J. Simon and J.J. Andre, *Molecular semiconductors*, eds J.M. Lehn and C.W. Rees, Springer-Verlag, Berlin, 1985, Chap. 3, pp. 112–116.
3 D. Wöhrle and D. Meissner, *Adv. Mater.*, 1991, **3**, 129.
4 Q. Liang, P. Zhao, J.W. Woo, Y.S. Park, L. Niu and F. Zhang, *Macromol. Res.*, 2010, **18**, 113–119.
5 R.O. Loutfy, A.M. Hor, C.K. Hsiao, G. Baranyi and P. Kazmaier, *Pure Appl. Chem.*, 1988, **60**, 1047.
6 K. Abe, H. Sato, T. Kimura, Y. Ohkatsu and T. Kusano, *Makromol. Chem. Phys.*, 1989, **190**, 2693.
7 B. Simic-Glavaski, *Phthalocyanine, properties and applications*, eds C.C. Leznoff and A.B.P. Lever, VCH Publications, New York, 1993, Vol. 3, Chap. 3, pp. 119–166.
8 S. Palacin, P. Lesieur, I. Stefanelli and A. Barraud, *J. Am. Chem. Soc.*, 1988, **110**, 83.
9 A. Rodriguez, M.E.S. Vergara, V.G. Montalvo, A. Ortis and J.R. Alvarez, *Appl. Surf. Sci.*, 2010, **256**, 3374–3379.
10 M.M. Nicholson, *In Phthalocyanine, Properties and Applications*, eds C.C. Leznoff and A.B.P. Lever, VCH Publications, New York, 1993, Vol. 3, Chap. 2, pp. 71–118.
11 T.J. Marks, *Angew. Chem. Int. Edit.*, 1990, **29**, 857.
12 A.W. Snow and W.R. Barger, *Phthalocyanine, properties and applications*, eds C.C. Leznoff and A.B.P. Lever, VCH Publications, New York, 1989, Vol. 1, Chap. 3, pp. 341–392.
13 Z. Odabaş, A. Altındal, A.R. Özkaya, B. Salih and Ö. Bekaroğlu, *Sensor. Actuat. B–CHem.*, 2010, **145**, 355–366.
14 J.F. Van der Pol, E. Neeleman, J.W. Zwikker, R.J.M. Nolte, W. Drenth, J. Aerts, R. Visser and S.J. Picken, *Liq. Cryst.*, 1989, **6**, 577.
15 M.K. Casstevens, M. Samoc, J. Pfleger and P.M. Prasad, *J. Chem. Phys.*, 1990, **92**, 2019.
16 M. Kato, Y. Nishioka, K. Kaifu, K. Kawamura and S. Ohno, *Appl. Phys. Lett.*, 1985, **46**, 196.
17 A.B.P. Lever, M.R. Hempstead, C.C. Leznoff, W. Lin, M. Menlik, W.A. Nevin and P. Seymour, *Pure Appl. Chem.*, 1986, **18**, 1467.
18 V. Duarte, D. Gasparutto, L.F. Yamaguchi, J.L. Ravanat, G.R. Martinez, M.H.G. Medeiros, P.D. Mascio and J. Cadet, *J. Am. Chem. Soc.*, 2000, **122**, 12622.
19 E.A. Lukyanets, *J. Porphyr. Phthalocya.*, 1999, **3**(6/7), 424–432.
20 I. Rosenthal, *Photochem. Photobiol.*, 1991, **53**, 859.
21 A. Erdoğmuş and T. Nyokong, *Polyhedron*, 2009, **28**, 2855.
22 I. Schulz, H.C. Mahler, S. Boiteux and B. Epe, *Mutat. Res.*, 2000, **461**, 145.
23 E. Kvam, K. Berg and H.B. Sten, *Biochim. Biophys. Acta.*, 1994, **9**, 1217.
24 A. Loupy, *Microwaves in organic synthesis*, ed V.C.H. Wiley, Weinheim, New York, 2002. Vol. 12, pp. 405–433.
25 E. Çelenk Kaya, H. Karadeniz and H. Kantekin, *Dyes and pigments*, 2010, **85**, 177–182.
26 F. Cataldo, *Dyes and pigments*, 1997, **34**, 75.
27 D.D. Dominguez, A.W. Snow, J.S. Shirk and R.S. Pong, *J. Porphyr. Phthalocya.*, 2001, **5**, 582–592.
28 H. Kantekin, E. Celenk and H. Karadeniz, *J. Organomet. Chem.*, 2008, **693**, 1353–58.
29 D. Wöhrle, M. Eskes, K. Shigehara and A. Yamada, *Synthesis-Stuttgart*, 1993, **2**, 194–196.