Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis and characterization of three covalently linked porphyrin-phthalocyanine pentamers with nucleophilic substitution

Samira Osati, Nasser Safari*, Parisa Rajabali Jamaat

Department of Chemistry, Faculty of Science, Shahid Beheshti University, G.C. Evin, 1983963113 Tehran, Iran

ARTICLE INFO

Article history: Received 9 September 2009 Received in revised form 8 March 2010 Accepted 11 March 2010 Available online 16 March 2010

Keywords: Phthalocyanine Porphyrin Oxy-bridge Pentamer Nucleophilic substitution Leaving group

ABSTRACT

In this paper the synthetic methods of three covalently linked porphyrin-phthalocyanine heteropentamers, containing four units of porphyrin linked to a central phthalocyanine (Mpor-LPc; M = 2H, Fe, L = Zn, Fe), are described. The synthetic strategy is on the basis of nucleophilic substitution reactions between [1,8,15,22-tetra nitro phthalocyanines] and [5-(4-hydroxy phenyl)-10,15,20-triphenyl porphyrins] as the phenolic alcohols. Porphyrins are linked with oxygen as spacer through meso position of phenyl group to phthalocyanines. These macromolecules were characterized by ¹H NMR, UV–Vis, IR, fluorescence and mass spectroscopy. The electronic absorption spectrums of the hetero-dyad systems changed significantly upon coupling and showed a great red shift in the phthalocyanine Q-bands. These changes confirm the electron-donating effects of the porphyrin units and the extension of conjugated π systems. The emission spectra of the products supports intramolecular energy and charge transfer between the sub-units.

© 2010 Elsevier B.V. All rights reserved.

Inorganica Chimica Acta

1. Introduction

Porphyrins and phthalocyanines represent two related groups of very versatile macrocyclic organic molecules. Metalloporphyrins are widely studied as biomimetic models for several biological redox processes [1], and have been extensively used in chemical, electrochemical [2] and photochemical analyses.

Metallophthalocyanines are widely used molecules in electrocatalyst [3], infrared sensors [4], and nonlinear optics [5] and photodynamic therapy agents [6,7]. They can also be useful for oxygen reduction in fuel cell technology [8].

Conjugates of porphyrins and phthalocyanines are very interesting structures for various reasons. The most important reason is that these macrocycles have complementary absorptions in the visible region and the emission spectra of phthalocyanines do not show significant overlap with those of the porphyrins. The fluorescence quantum yields of phthalocyanines are 6–10 times higher than porphyrins [9]. Another reason is the stability of these molecules. Phthalocyanines are generally more stable and more rigid than porphyrins, so they oxidize harder. As a result the electrochemical oxidation of a porphyrin can be performed in the presence of phthalocyanines. So these conjugates are good choices for usage in molecular photonics, catalysis and light harvesting architectures with a good spectral coverage in the blue and red wavelengths [9]. Different synthetic strategies have been used to prepare multi porphyrin-phthalocyanine arrays. These methods are based on electrostatic interactions in molecules with opposite charges, host–guest interactions [10], the axial coordination [11] and covalent linking's by using functional groups [12–16].

The covalent linking of phthalocyanines to porphyrins was first achieved by Gaspard and co-workers [17]. A dimmer of these compounds with one porphyrin unit linked to a phthalocyanine unit was shown to exhibit interesting charge transfer properties [18]. Phthalocyanine-porphyrin nonamers as a mixture of isomers of tetra substitution of porphyrin dimmers have also been prepared [19]. These arrays are stable enough against oxidant or reductant agents [20,21] and can be used as multi-nuclear catalysts.

In this paper we report the synthesis, characterization and spectral properties of covalently linked pentamers, one phthalocyanine and four porphyrins linked through an oxy-bridge. Oxygen atoms fully conjugate the five major π systems and improve the efficiency of the electron and energy transfer processes.

The synthesis started from the corresponding functionalized metalloporphyrins (with one OH group) and metallophthalocyanines (with four NO₂ group) instead of the synthetic route involving the self-cyclization reaction of phthalonitrile derivatives which Nyokong and co-workers had been used [21]. For synthesis of nitrophthalocyanines (**2a** and **2b**) we used 3-nitrophthalonitrile instead of 4-nitrophthalonitrile used in Nyokong's works. This compound broaden UV–Vis spectrum coverage of pentamers and larger Q-bands shifts about 50–78 nm observed that have not been reported before. Our method gives high yields relative to starting



^{*} Corresponding author. Tel.: +98 21 22401765; fax: +98 21 22403041. *E-mail address:* n-safari@cc.sbu.ac.ir (N. Safari).

^{0020-1693/\$ -} see front matter \odot 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2010.03.022

used porphyrins and phthalocyanines. This synthetic strategy can be applied to prepare mixed metal arrays with high yields and will be useful for the preparation of other substituted phthalocyanines and has not been reported previously.

2. Experimental

2.1. General

UV–Vis spectra were recorded on a Shimadzu UV–Vis 2100 spectrophotometer. The IR spectrums were recorded on a Bomem-MB102 FT-IR spectrometer. ¹H NMR and ¹³C NMR spectra were recorded using a Bruker 300 MHz NMR. MALDI-TOF measurements were performed with a Kratos Kompakt mass spectrometer. A nitrogen laser (337 nm) was used for desorption and ionization with an accelerating voltage of 20 kV. Ions were detected as positive on a time-of-flight mass detector in the reflector mode. Dithranol was used as a matrix and LiBr was used as cationating agent. Elemental analyses were performed on a LECO CHNS 932 instrument. Fluorescence emission spectra were performed with a Varian Cary Eclipse spectrofluorometer.

2.2. Chemicals

Pyrrole, benzaldehyde, 4-hydroxy benzaldehyde, potassium carbonate, iron (II) chloride, zinc acetate, silica gel 60 for chromatography and DMF were purchased from Merck.

1,8,15,22-Tetra nitro zinc (II) phthalocyanine (**2a**) and 1,8,15,22-tetra nitro iron (II) phthalocyanine (**2b**), were synthesized as reported in the literature [22]. All solvent were dried using standard methods prior to use.

2.3. Synthesis

2.3.1. [5-(4-Hydroxy phenyl)-10,15,20-triphenyl porphyrin] (**1a**) and [5-(4-hydroxy phenyl)-10,15,20-triphenyl porphyrin] iron (III) chloride (**1b**)

A mixture of 4-hydroxybenzaldehyde (10 mmol, 1.25 g) and benzaldehyde (30 mmol, 3 cm³) were added to 80 cm³ propionic acid, under nitrogen atmosphere. Pyrrole (40 mmol, 2.8 cm³) was added and the resulting mixture was refluxed for 1 h. After cooling to room temperature, the mixture was filtered and washed three times with hot water. Column chromatography on silica gel was performed with dichloromethane/n-hexane (1:1) as eluent The first major cut was TPP and the second cut was found to be (1a) [26]. Evaporation of the solvent resulted 0.6 g (10%) of a purple solid **1a**. UV–Vis (DMF): λ_{max}/nm (log ε): 420(5.4), 517(4.4), 550(4.1), 590(4.0), 654(4.2). ¹H NMR (300 MHz, DMSO-d₆, 25 °C) : δ, ppm -2.91 (s, 2H, N-H), 7.21-7.23 (d, 2H, phenyl H), 7.74-7.75 (m, 9H, phenyl H), 8.01-8.05 (d, 2H, phenyl H), 8.25-8.28 (d, 6H, phenyl H), 8.75–8.78 (d, 6H, pyrrole H), 8.90–8.92 (d, 2H, pyrrole H), 9.96 (s, 1H, OH). MALDI-TOF-MS: *m*/*z*: 636.36 [M+Li-H]⁺. Anal. Calc. for C44H30N4O: C, 83.82; H, 4.75; N, 8.88. Found: C, 83.75; H, 4.79; N, 8.91%.

A mixture of **1a** (2 mmol, 1.26 g) and iron (II) chloride (4 mmol, 0.795 g) in 30 cm³ dimethylformamide DMF was heated at 100 °C for 2 h while stirring under nitrogen for preventing μ -oxo dimer formation [23]. Removal of DMF by evaporation resulted in a purple solid that was washed with an adequate amount of water in order to eliminate the of extra iron chloride (II). The MALDI-TOF mass spectra showed only a monomeric molecular ion peak, indicating absence of μ -oxo dimer. The crude product (**1b**) was recrystallized from dichloromethane with methanol and produced 87% yield. UV–Vis (DMF): λ_{max} /nm (log ε): 419(5.2), 512(4.5), 588(4.3). ¹H NMR (300 MHz, DMSO-d₆) paramagnetic, δ 72.8 (H pyrrole), 80.1

(H pyrrole) with the ratio of 3:1.¹H NMR (300 MHz, CDCl₃) paramagnetic, 81.2 (H pyrrole), 12.2 (meta H phenyl), 13.4 (meta H phenyl), 6.3 (para H phenyl), 8.0 (ortho H phenyl). MALDI-TOF-MS: m/z: 690.15 [M+Li-H-Cl]⁺. *Anal.* Calc. for C₄₄H₂₈N₄OFeCl: C, 73.42; H, 3.89; N, 7.78. Found: C, 73.21; H, 3.92; N, 7.71%.

2.3.2. Tetrakis [5-phenoxy-10,15,20, triphenyl porphyrin] zinc (II) phthalocyanine (**3a**)

A mixture of **2a** (0.025 mmol, 0.02 g), **1a** (0.2 mmol, 0.126 g) and dry K_2CO_3 (0.2 mmol, 0.027 g) in 20 cm³ dry DMF was refluxed under nitrogen atmosphere for 6 h, and then K₂CO₃ was separated by filtration. After the solvent evaporated, column chromatography on basic alumina was performed. CH₂Cl₂ was used as an eluent and nonreacted porphyrins were separated as the first cut. Toluene: DMF mixture was used as a more polar solvent. By using solvent mixtures that contained increasingly 10-25% DMF two separated band were isolated. The first was a mixture of statistic products and the second cut was the desired product with 52% yield. UV-Vis (DMF): λ_{max}/nm (log ε): 421(5.4), 517(4.4), 550(4.1), 589(4.0), 654(4.2), 722(4.4). ¹H NMR (300 MHz, DMSO-d₆) the spectrum was similar to **1a** in addition to δ : 7.6–7.6 (phthalocyanine H). IR (KBr): v_{max} , cm⁻¹: 1261(aromatic C–O–C). MALDI-TOF-MS: m/z: 3097.05 [M+Li-H]⁺. Anal. Calc. for C₂₀₈H₁₂₈N₂₄O₄Zn: C, 80.80; H, 4.14; N, 10.86. Found: C, 80.74; H, 4.18; N, 10.91%.

2.3.3. Tetrakis [5-phenoxy-10,15,20, triphenyl porphyrin iron (III) chloride] zinc (II) phthalocyanine (**3b**)

A mixture of **2a** (0.025 mmol, 0.02 g), **1b** (0.2 mmol, 0.136 g) and dry K_2CO_3 (0.2 mmol, 0.027 g) in 20 cm³ DMF was refluxed under nitrogen atmosphere for 6 h and then K_2CO_3 was separated by filtration. After the solvent evaporated, column chromatography on basic alumina was performed according to the method used for **3a** and **3b** with 55% yield. UV–Vis (DMF): λ_{max}/nm (log ε): 419(5.4), 572(4.3), 512(4.2), 750(4.5), ¹H NMR (300 MHz, DMSO-d₆) paramagnetic, δ 79.24 (6H, pyrrole H), 72.10 (2H, pyrrole H). ¹H NMR (300 MHz, CDCl3), δ 81.4 (8H, pyrrole H), 13.5 (3H, meta phenyl H), 12.8 (1H meta phenyl H), 12.3 (3H, meta phenyl H), 11.7 (1H meta phenyl H). IR (KBr): ν_{max} , cm⁻¹: 1261 (aromatic C–O–C). MALDI-TOF-MS: m/z: 3324.12 [M+3Li–3H–4Cl]⁺ Anal. Calc. for C₂₀₈H₁₂₀N₂₄O₄Cl₄Fe₄Zn: C, 72.43; H, 3.47; N, 9.74. Found: C, 72.51; H, 3.49; N, 9.79%.

2.3.4. Tetrakis [5-phenoxy-10,15,20, triphenyl porphyrin iron (III) chloride] iron (II) phthalocyanine (**3c**)

A mixture of **2b** (0.025 mmol, 0.02 g), **1b** (0.2 mmol, 0.136 g) and dry K_2CO_3 (0.2 mmol, 0.027 g) in 20 cm³ DMF was refluxed under nitrogen atmosphere for 6 h. The solvent evaporated and column chromatography was performed according to the method used for **3a** and **3c** collected in 50% yield. UV–Vis (DMF): $\lambda_{max}/$ nm (log ε): 419(5.5), 573(4.6), 619(4.4), 652(4.5) 725(4.6). ¹H NMR (300 MHz, DMSO-d₆) paramagnetic, δ 83.5 (8H, pyrrole H). IR (KBr): ν_{max} , cm⁻¹: 1261(aromatic C–O–C). MALDI-TOF-MS: *m*/*z*: 3302.88 [M+Li–H–4CI]⁺. *Anal.* Calc. for C₂₀₈H₁₂₀N₂₄O₄Cl₄Fe₅: C, 72.63; H, 3.48; N, 9.77. Found: C, 72.65; H, 3.49; N, 9.76%.

3. Results and discussion

In this article we used nucleophilic aromatic substitution reactions for the synthesis of substituted phthalocyanines in terms of the leaving groups and nucleophiles used. NO_2 is a good leaving group for nucleophilic aromatic substitution reactions. In the S_NAr mechanism the rate determining step involves formation of a tetrahedral intermediate and its formation is promoted by the leaving groups having strong electron withdrawing effects such as NO_2 [24]. Both aliphatic [25] and phenolic alcohols have been added to nitrophthalonitrile successfully via nucleophilic displacement of the nitro group. The nitro group has also been substituted with sterically hindered aryl alcohols using K₂CO₃ as a base and DMF in relatively high yields. Based on this strategy we used hydroxyl porphyrins **1a** and **1b**, modified phenolic alcohols, as nucleophiles and tetra substituted nitro phthalocyanines to synthesize the Porphyrin-phthalocyanine pentamers.

The synthetic route for the compounds presented in this work is shown in Fig. 1. The compounds are abbreviated as indicated in Fig. 1 and experimental section. H₂TPP(OH) (1a) was synthesized and metallated using iron (II) chloride in nitrogen atmosphere to obtain FeTPPCl(OH) (1b). These compounds were characterized by IR, UV-Vis, elemental analysis, MALDI-TOF mass spectroscopy as well as ¹H NMR spectroscopy. In the ¹H NMR spectrum of **1a**, the OH on the phenoxy ring caused the splitting of pyrroles and phenyl protons as is observable in Fig. 2. Pyrrole resonances in compound 1a splitted into two sets with ratio of 1:3 at 8.7-8.9 ppm similar to the place reported for TPPH₂ [26]. Unsubstituted phenyl protons were seen at the same place for TPPH₂ on the three phenyl rings, whereas proton signals on the phenoxy ring $(H_2$ and H_3 in Fig. 1) were shifted to higher fields. The splitting pattern and integration of the signals are consistent with the structure shown for compound **1a** in Fig. 2. Paramagnetic ¹H NMR is very informative for characterization of **1b** and the ¹H NMR spectrum of DMSO-d₆ solution of **1b** is presented in part A of Fig. 3. The Presence of paramagnetic iron (III) in 1b leads to the splitting of broad pyrrole position protons to two sets with 1:3 ratios at 80.1 ppm and 72.8. However the ¹H NMR spectrum of **1b** in a CDCl₃ solution shows all pyrrole protons at 81.4 ppm at 25 °C consistent with the pyrrole position of FeTPPCI [27]. Furthermore the phenyl meta protons are splitted into two sets that confirms the hydroxylation of one phenyl ring in compound **1b**. The region of 11.7–13.5 is due to meta protons of phenyls for high spin iron (III) complex of tetra phenyl porphyrin. Phenyl groups are perpendicular on the porphyrin ring, so the presence of (Cl) as an axial ligand causes different conditions for the two parts of protons. Therefore meta protons on the phenyl groups were splitted into two sets at 12.3 ppm and 13.5 ppm. For compound **1b** the same protons on the phenoxy group appeared at 12.8 and 11.7 with ratio of 3:1 and a small shift to higher fields relative to TPP.

 $(ZnPc-(H_2TPP)_4)$ (**3a**) was synthesized using the reaction of **1a** with 2a in the presence of dry K_2CO_3 and DMF in 52% yield relative to 2a. UV-Vis monitoring shows the reduction of 2a Q-bands at 672 nm and the growth of a new band at 722 nm. Our goal was to prepare a phthalocyanine substituted with four porphyrins. Since the commonly numbered 1- or 4-positions in phthalocyanines are known to be passive of high steric hindrance for further substitutions we used an excess of porphyrins to complete the reaction. The reaction was performed with 4:1 ratio (stochiometric ratio) of porphyrin to phthalocyanine. Note, the final yields in the stochiometric ratio of porphyrin to phthalocyanine were just 5% less than the reported excess ratio. Therefore it seems this synthesis strategy is very efficient for coupling porphyrin to phthalocyanines and has an advantage over previous methods, in that overall yields are around 50%, while in other methods reported in literature, the vields are less.

The ¹H NMR spectrum of **3a** indicated combinatory signals of their component **1a** and **2a** with elimination of signal due to the phenoxy OH group. A broad peak from 7 to 8 ppm and a signal at 7.6 was due to **2a**. The shift of ZnPc peaks to higher field confirmed the electron-donating effects of porphyrin to phthalocyanine. The UV–Vis spectrum of **3a** showed characteristic peaks of porphyrin and phthalocyanines. However a large shift of about 50 nm was seen for the Q band of ZnPc in compound **3a** relative to the mixture of **1a** and **2a**, Table 1 (from 672 nm for ZnPc alone to 722 nm for



Fig. 1. Synthetic route in preparing porphyrin-phthalocyanine pentamers. 3a is formed from reaction of 1a and 2a, 3b from reaction of 1b and 2a and 3c from reaction of 1b and 2b.



Fig. 2. (A) ¹H NMR spectrum of **1a** in DMSO-d₆ solution at room temperature, (B) assignment of **1a** protons.



Fig. 3. Paramagnetic ¹H NMR spectrum of 1b (A) and 3b (B) in DMSO-d₆ solution at room temperature. H₇ and H₈ are pyrrole position signals shown in part B of Fig. 2.

Table 1 λ_{max} nm/(log ε) due to Q-bands of phthalocyanines before and after reaction and related shifts in UV–Vis spectrum at concentration of 10⁻⁵ mol/l in DMF.

Phthalocyanines	Q-band before reaction	Q-band after reaction	Total shift
2a	672 nm(4.8)	(3a) 722 nm(4.4)	50 nm
2a	672 nm(4.8)	(3b) 750 nm(4.5)	78 nm
2b	666 nm(4.9)	(3c) 725 nm(4.6)	59 nm

ZnPc in **3a**). This observation suggests that presence of porphyrins on the three position on phthalocyanine confer more electrondonating effects on metallophthalocyanines complexes relative to other isomers in literature. The IR spectrum of this compound showed the elimination of the NO₂ vibration at 1531 cm⁻¹ and the C–N stretching band at 1336 cm⁻¹ in addition to the growth of the peak of aromatic ether at 1261 cm⁻¹ and the reduction of the OH peak at about 3300 cm⁻¹ as shown in Fig. 4. Another indication of this structure being correct was obtained from the mass spectrum which had a molecular ion peak at m/z: 30 905.7. [M+Li–H]⁺ (Fig. 5).

 $(ZnPc-(Fe (TPP)_4) (3b)$ as a mixed metal pentamer was synthesized with 55% yield relative to 2a and characterized by IR, ¹H NMR, UV–Vis and mass spectroscopy. The IR spectrum shows the elimination of NO₂ peaks at 1529 cm⁻¹. UV–Vis indicates a red shift of about 78 nm from 672 nm for ZnPc in the mixture of 1b and 2a to 750 nm for ZnPc in 3b (Fig. 6). The large red shift confirms electron communication between the porphyrin and phthalocyanines rings. Paramagnetic ¹H NMR spectrum of 3b is shown in part B of Fig. 3. The pyrrole protons were again splitted into two sets as expected. Opposite to 1b which was an iron porphyrin monomer, intensity patterns of the pyrrole rings were reversed



Fig. 4. FT-IR spectrum of (A) mixture of 1a and 2a before reaction and (B) 3a after reaction is complete.

in pentamer **3b**. This showed electronic effects of ZnPc ring to the porphyrin which affected the position of the pyrrole rings. The MALDI-TOF mass spectrum also confirmed the formation of the pentamer **3b** with a molecular ion peak at m/z: 3324.12 [M+3Li-3H-4Cl]⁺. The Lithium adducts derived from exchange of protons with Lithium ions, and this has been observed previously [28]. The MALDI-TOF mass spectrum of **1b**, **3b** and **3c** shows the mass ion peak without axial chloride such as similar structures reported in literature however elemental analysis proved presence of four axial chlorides [29,30]. Porphyrin μ -oxo dimmers, having sterically hindered macrocycles, are not readily formed. The steric hindrance of iron porphyrins in pentamers **3b** and **3c** prevent the



Fig. 5. MALDI-TOF MS spectrum of **3a** with a molecular ion peak at m/z 3097.05 $[M+Li-H]^+$.



Fig. 6. UV–Vis spectrum of (A) mixture of **1b** and **2a** in molar ratio of 4:1 before reaction and (B) their product **3b** after reaction both in DMF at concentration of 10^{-5} mol/l.

formation of μ -oxo dimmers as indicated by MALDI-TOF mass spectra [31].

(FePc-(FeTPP)₄) (**3c**) with five Fe center synthesized with 50% yield relative to **2b** and characterized by IR (elimination of NO₂ vibration at 1536.7 cm⁻¹ and C–N stretch at 1353 cm⁻¹ and growth of aromatic ether peak at 1261 cm⁻¹), UV–Vis (red shift about 59 nm from 666 nm of FePc alone to 725 nm for FePc in **3c**) and ¹H NMR spectroscopy. The Paramagnetic ¹H NMR spectrum of **3c** in DMSO-d₆ solution at pyrrole proton region showed a broad peak at 83.59 ppm about 3 ppm more downfield compared to TPPFeCI [24]. The broadness of the peak is due to the overlapping of two sets of pyrrole peaks. The MALDI-TOF mass spectrum of the precipitate clearly shows the mass ion peak at *m*/z 3302.88 corresponding to [M+Li–H–4Cl]⁺.

The emission spectra of compounds **3a**, **3b** and **3c** in 405 nm (at a vibronic band near the soret band of the porphyrin) and 650 nm (near the Q band of phthalocyanine) were analyzed. There was a quenching of singlet excited states of **1a**, **1b**, **2a** and **2b** when each of them was selectively excited in pentamers. Energy transfer from phthalocyanine to porphyrin is impossible because LUMO of porphyrin is higher than phthalocyanine but the reverse process can occur. So **2a** and **2b** quenching was a combination of both charge transfer and energy transfer, but the quenching of **1a** and **1b** moiety in pentamers was only due to charge transfer. These observations confirm high interaction between porphyrin and phthalocyanine moieties.

4. Conclusion

In this work, we synthesized three conjugated phthalocyanine– porphyrins that are connected through meso phenyl group with etheric spacers. In our method, functionalized metalloporphyrins and metallophthalocyanines were used and mixed metal arrays were prepared. Characterization by UV–Vis, ¹H NMR, MALDI-TOF-MS, IR, elemental analysis and Fluorescence spectroscopy confirmed synthesis of these pentamers.

Acknowledgments

This study has been supported by Iranian National Science Foundation and Research and Graduate Study Councils of Shahid Beheshti University for financial support. We would like to thank Dr. Farhad Raofie for his assistance with the MALDI-TOF spectral analysis.

References

- M. Perez-Morales, G. de Miguel, E. Munoz, M.T. Martin-Romero, L. Camacho, Electrochim. Acta 54 (2009) 1791.
- [2] K. De Wael, A. Adriaens, Electrochim. Acta 53 (2008) 2355.
- [3] C. Song, L. Zhang, J. Zhang, J. Electroanal. Chem. 587 (2006) 293.
- [4] G. Mbambisa, T. Nyokong, Polyhedron 27 (2008) 2799.
- [5] Y. Liu, S.M. O'Flaherty, Y. Chen, Y. Araki, J. Bai, J. Doyle, W.J. Blau, O. Ito, Dyes Pigm. 75 (2007) 88.
- [6] R.W.Y. Sun, C.M. Che, Coord. Chem. Rev. 253 (2009) 1682.
- [7] N. Nishiyama, Y. Nakagishi, Y. Morimoto, P.S. Lai, K. Miyazaki, K. Urano, S. Horie, M. Kumagai, S. Fukushima, Y. Cheng, W.D. Jang, M. Kikuchi, K. Kataoka, J. Controlled Release 133 (2009) 245.
- [8] J. Ma, Y. Liu, P. Zhang, J. Wang, Electrochem. Commun. 10 (2008) 100.
- [9] S.I. Yang, J. Li, H.S. Cho, D.K. Bocian, D. Holten, J.S. Lindsey, J. Mater. Chem. 10 (2000) 283.
- [10] X. Leng, C.F. Choi, P.C. Lo, P. Ng, Org. Lett. 9 (2007) 231.
- [11] E.A. Ermilov, S. Tannert, T. Werncke, M.T.M. Choi, D.K.P. Ng, B. Röder, Chem. Phys. 328 (2006) 428.
- [12] H. Ali, J.E. Van Lier, Tetrahedron Lett. 50 (2009) 1113.
- [13] A.R.M. Soares, M.V. Martiinez-Diaz, A. Bruckner, A.M.V.M. Pereira, J.P.C. Tome, C.M.A. Alonso, M.A.F. Faustino, M.G.P.M.S. Neves, A.C. Tome, A.M.S. Silva, J.A.S. Cavaleiro, T. Torres, D.M. Guldi, Org. Lett. 9 (2007) 1557.
- [14] A. Ambroise, R.W. Wagner, P.D. Rao, J.A. Riggs, P. Hascoat, J.R. Diers, J. Seth, R.K. Lammi, D.F. Bocian, D. Holten, J.S. Lindsey, Chem. Mater. 13 (2001) 1023.
- [15] M. Durmus, J.Y. Chen, Z.X. Zhao, T. Nyokong, Spectrochim. Acta, Part A 70 (2008) 42.
- [16] S. Gaspard, C. Giannotti, P. Maillard, C. Schaeffer, T.H. Tran-Thi, J. Chem. Soc., Chem. Commun. 16 (1986) 1239.
- [17] T.H. Tran-Thi, C. Desforge, C. Thiec, S. Gaspard, J. Phys. Chem. 93 (1989) 1226.
- [18] J. Li, J.S. Lindsey, J. Org. Chem. 64 (1999) 9101.
- [19] Z. Zhao, T. Nyokong, M.D. Maree, Dalton Trans. 23 (2005) 3732.
- [20] Z. Zhao, K.I. Ozoemena, M.D. Maree, T. Nyokong, Dalton Trans. 7 (2005) 1241.
 [21] Z. Zhao, A.O. Ogunsipe, M.D. Maree, T. Nyokong, Porphyrins Phthalocyanines 9
- (2005) 186. [22] A. Shaabani, N. Safari, A. Bazgir, F. Bahadoran, N. Sharifi, P.R. Jamaat, Synth.
- [22] A. Shaabani, N. Safari, A. Bazgir, F. Banadoran, N. Sharin, P.K. Jamaat, Synth. Commun. 33 (2003) 1717.
- [23] E.B. Fleischer, J.M. Palmer, T.S. Srivastava, A. Chatterjee, J. Am. Chem. Soc. 93 (1971) 3162.
- [24] E. Ben-Hur, W.S. Chan, K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 15, 2003, p. 26.
- [25] Z. Biyikioglu, I. Acar, H. Kantekin, Inorg. Chem. Commun. 11 (2008) 630.
- [26] E. Ben-Hur, W.S. Chan, K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 5, 2003, p. 47.
- [27] E. Ben-Hur, W.S. Chan, K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 5, 2003, p. 121.
- [28] J. Su, M. Mrksich, Langmuir 19 (2003) 4869.
- [29] M. Kimura, T. Shiba, M. Yamazaki, K. Hanabusa, H. Shirai, N. Kobayashi, J. Am. Chem. Soc. 123 (2001) 5636.
- [30] T.E. Clement, D.J. Nurco, K.M. Smith, Inorg. Chem. 37 (1998) 1150.
- [31] K.M. Kadish, M. Autret, Z. Ou, P. Tagliatesta, T. Boschi, V. Fares, Inorg. Chem. 36 (1997) 204.