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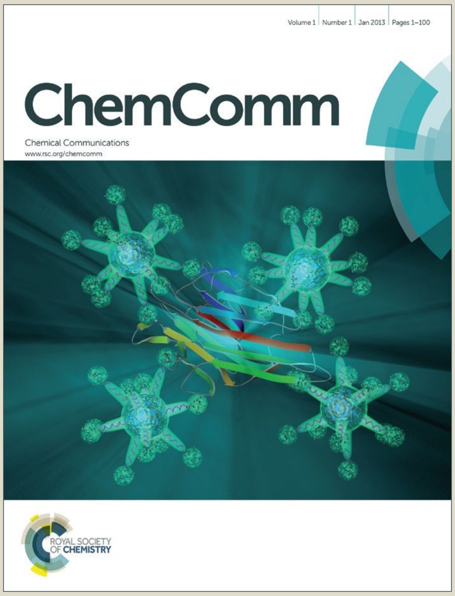

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β-Octakis(methylthio)porphycenes: Synthesis, Characterisation and Third Order Nonlinear Optical Studies†

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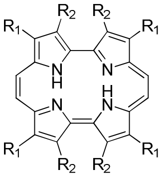
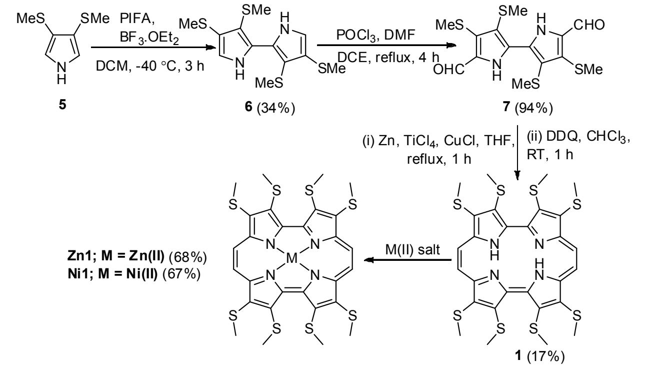
A novel electron deficient *β*-octakis(methylthio)porphycene, along with its Zn(II) and Ni(II) derivatives were synthesized for the first time. The macrocyclic structure exhibits core ruffling with largely red shifted absorption band (~750 nm) and also a large enhancement in the third order nonlinear optical response.

Porphycene is the first constitutional isomer of much revered porphyrin as has been reported by Vogel.[1] Owing to its reduced symmetry, this macrocycle displays enhanced absorption in the red region. This feature drew wide attention of researchers to seek its potential utility as an effective photosensitizer for photodynamic therapy.[2] However, investigation of its potential as nonlinear optical (NLO) materials is still at a rudimentary stage due to the difficulties in the synthesis and further functionalization of appropriately substituted porphycenes.[2,3] In this regard, development of new strategies for synthesis and functionalization is critical in the study of porphycene. Besides, porphyrins containing electron-donating (OMe) and withdrawing substituents (Cl) on adjacent *β*-pyrrolic positions display higher TPA cross-section compared to that substituted with electron-donating substituents at all of their *β*-positions.[4] As the structure and photophysical properties of porphycenes are more sensitive to the substituents compared to porphyrins, it is also worth examining whether the same concept could be viable in the third order NLO properties.



2; $R_1 = R_2 = Et$
3; $R_1 = R_2 = OMe$
4; $R_1 = Et, R_2 = CF_3$

To this end, we synthesized the first porphycene with electron withdrawing substituents at all *β*-positions, namely *β*-octakis(methylthio)porphycene **1**. In particular, we introduce the use of SMe group in our synthetic protocol, which serves as a good protecting group as well as a good leaving group for S_NAr and catalytic organic transformations, which may enhance the scope of further substitution on porphycene periphery.[5] Moreover, the photophysical dynamics and the third order NLO responses of the freebase porphycene along with its Ni(II)-complex were explored by comparing with those of the corresponding *β*-octaethyl **2**[6] and *β*-octamethoxy **3**[7] analogues to evaluate the substituent effect.



Scheme 1 Synthesis of β-octa(methylthio)porphycenes.

The synthesis of porphycene **1** was achieved by modifying a previously developed method in our group (Scheme 1).[7] Oxidative coupling of 3,4-di(methylthio)pyrrole **5**[8] with hypervalent iodine(III) reagent [bis(trifluoroacetoxy)iodo]-benzene (PIFA) as oxidant and TMSBr as Lewis acid at -40 °C led to the formation of bipyrrole **6** in a very poor yield, probably due to the relatively electron deficient nature of **5** compared with 3,4-dimethoxypyrrole.[7,9] In order to activate the electron deficient pyrrole **5**, we performed PIFA coupling with a relatively strong Lewis acid (BF_3.OEt) under the same reaction condition, to obtain the desired bipyrrole **6** in 34% yield. Unlike tetramethoxy-2,2'-bipyrrole[7], bipyrrole **6** was found to be quite stable and hence could be purified by silica gel column chromatography and stored at -20 °C for months. The bipyrrole **6** was then subjected to Vilsmeier-Haack formylation to provide the dialdehyde **7** in 94% yield, whose structure was further confirmed by X-ray crystallography (Fig. S11 in the ESI†). Finally, McMurry coupling of **7** with Zn/$TiCl_4$ in the presence of CuCl under reflux condition provided the dihydroporphycene as the coupling product, which undergoes slow oxidation under ambient condition, suggesting the electron deficient nature of the desired porphycene **1**. After McMurry coupling followed by usual workup, the resultant yellow orange residue was dissolved in $CHCl_3$ and subjected to oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at room temperature, which finally led to the desired porphycene **1** in 17% yield. The freebase porphycene was further converted to its Zn(II) and Ni(II) complexes in 68 and 67% yield, respectively. Notably, the **Zn1** complex slowly undergoes demetallation in solution indicating its labile nature. All the compounds were characterized by standard spectroscopic techniques. Also, the ^{1}H NMR spectrum of **1** displays *meso* protons at 9.68 ppm, which is about 0.31 ppm downfield shifted compared to **4** (9.37 ppm)[10], and this trend is again observed for the imino protons resonating at 2.98 ppm for **1**, which is 0.65 ppm downfield shifted compared to **4** (2.33 ppm)[10], indicative of the electron deficient nature of the former.

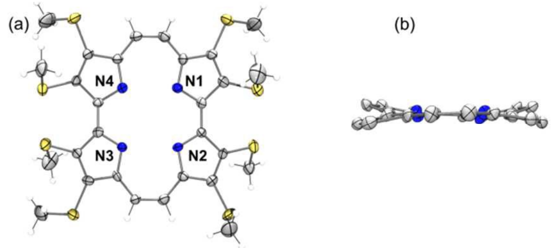


Fig. 1 Molecular structure of **1** (a) front view and (b) side view drawn in 35% probability level. In side view all hydrogen atoms and methylthio groups were removed for clarity. Colour code: C, grey; H, white; N, blue; S, yellow.

The solid state structure of porphycene **1** could also be unequivocally elucidated by single crystal X-ray diffraction analysis (Fig. 1). The replacement of eight oxygen atoms of **3** with relatively bulkier sulphur atoms is clearly revealed, leading to the twisting of pyrrole moieties along Cα-Cα′ axis of the bipyrrole units. Similar to porphycene **4**, a saddle-like distorted structure is observed for **1**, arising from lone pair-lone pair repulsion between the adjacent sulphur atoms at 3,6- and 13,16-positions.[10] The average torsion angle between the two adjacent pyrroles along the Cα-Cα′ axis of bipyrrole is 24.10°, which is smaller than that of porphycene **4** (29.50°). The degree of distortion can also be measured by displacement of the β-C's in the pyrrolic moieties from the mean plane drawn through four core nitrogens. The maximum displacement observed in **1** is 0.544 Å, which is again much smaller compared to that of **4** (0.976 Å).[10] These data clearly indicate weaker nonbonding interaction between the SMe substituents at the inner β-positions compared to the CF_3 units in **4**, hence making it relatively more planar. The core of porphycene **1** exhibits a near-square type geometry like other β-octa-substituted analogues.

The UV-Vis absorption spectrum (Fig. 2) of porphycene **1** in $CHCl_3$ reveals striking differences from those of other β-octa-substituted porphycenes reported so far, consisting of a split Soret band (i.e. the shoulder at the higher-energy side more obvious) with the absorption maxima at 411 nm and a broad Q-band composed of three merged sub-bands. Moreover, unlike other similarly substituted porphycenes, the band at the middle of the three sub-structures shows the maximum intensity. This unusual type of Q-band originates from the rhodifying effect of eight electron-deficient methylthio group.[8a]

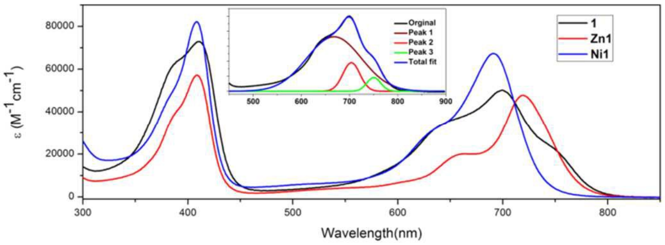


Fig. 2 The UV-Vis absorption spectra of **1**, **Zn1** and **Ni1**. Inset contains the Gaussian deconvolution of the Q-bands of **1** in $CHCl_3$ at 25 °C.

The lowest-energy band appeared at ~750 nm (deconvoluted), which is ~26 nm red shifted compared to porphycenes **4**,[10] clearly indicating the more electron deficient nature of **1**. Further, macrocycle **1** displays a very intense Q-band (intensity ratio of Q-band/Soret maxima 0.69), which has not previously been noticed in other freebase porphycenes. This highlights the unique substituent effect in **1** with electron deficient substituents and may partly be attributed to S-S interactions. Notably, the Soret band of **1** is red shifted compared to other β-octa-substituted porphycenes, again reflecting its electron deficient behaviour.[7,10,11] The UV-Vis absorption spectra of **Zn1** and **Ni1** display slightly blue shifted Soret bands (409 and 408 nm, respectively) and blue shifted Q-bands (719 and 691 nm, respectively) compared to **1**. Similar to freebase porphycene **1**, intense Q-bands were also observed for both **Zn1** and **Ni1** (Q-band/Soret maxima for **Zn1**, 0.83 and **Ni1**, 0.82). Porphycene **1** and its Zn(II) derivative display very weak fluorescence with maxima at 754 and 765 nm, respectively (Fig. S13 in the ESI†). Although all these molecules possess intense absorption in the NIR region, only **Zn1** could convert molecular oxygen to reactive singlet oxygen, albeit with very poor efficiency (ϕ_Δ = 0.04) in aerated toluene, thereby indicating their inability to act as a photosensitizer (Fig. S15 in the ESI†).

It has widely been established that the most important factor that contributes to the enhancement of two-photon absorption (TPA) is the extension of π-conjugation network. Another effective factor that is proposed to enhance TPA is charge-transfer interactions.[12] In this context, β-octaethyl, β-octamethoxy and β-octamethylthio analogues were employed to examine the effect of charge-transfer interactions on TPA behaviors[13] by the Z-scan technique in toluene from 1200 to 1500 nm, where the contribution from one-photon absorption (OPA) is negligible (Fig. 3 and S16 in the ESI†). The TPA profiles revealed spectral features that are in good agreement with the band structure of the lowest OPA band. The maximum TPA cross-sections of porphycenes **1**, **2** and **3** were measured to be 370, 110 and 230 GM at 1400, 1300 and 1200 nm, respectively. The maximum TPA cross-sections of their corresponding Ni(II) complexes, i.e. **Ni1**, **Ni2** and **Ni3**, were measured to be 270, 130 and 210 GM at 1400, 1200 and 1200 nm, respectively. The octamethoxyporphycenes **3** and **Ni3** display larger TPA cross-sections than their corresponding octaethyl analogues, probably due to facile intramolecular charge transfer (ICT) ability of methoxy groups. While porphycene **1** and its Ni(II) complex are expected to exhibit smaller TPA cross-sections than other porphycene analogues owing to their electron-deficient character,[14] they were found to display unexpectedly larger TPA cross-sections than other porphycene analogues. It is known that the numbers of π-electrons and/or the molecular geometry associated with static and dynamic polarizability are the determining factors in controlling NLO response in simple molecules.[15] Therefore, these unexpected results may be attributed to the heavy atom effect of the S atoms in the methylthio substituents and their greater polarizability in the excited state.[16] Notably, all octasubstituted porphycenes studied have much higher TPA cross-section values than previously reported 2,7,12,17-tetraphenyl-porphycene (14 GM at 1100 nm) at similar wavelengths.[3c]

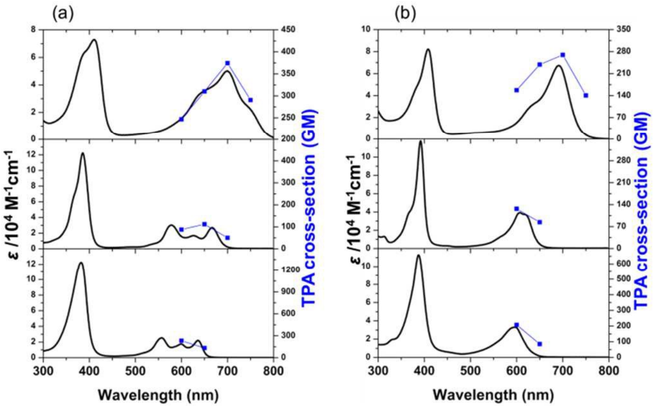


Fig. 3 OPA (solid line) and TPA (point line) of (a) freebase porphycenes and (b) their corresponding Ni(II)-complexes: **1**, **Ni1** (top), **2**, **Ni2** (middle) and **3**, **Ni3** (bottom) in toluene. The TPA spectra are displayed at $\lambda_{ex}/2$ for comparison with the OPA spectra.

The excited-state dynamics of porphycenes **1**, **2**, **3**, and their Ni(II) complexes were probed by femtosecond transient absorption (TA) spectroscopy (Figs. 4, S17 and S18 in the ESI†). The TA spectra of these compounds exhibit ground state bleaching signals whose spectral features well correspond to their ground-state absorption bands. In the case of porphycene **2**, we could observe a single exponential decay time component (450 ps) attributable to the singlet excited state lifetime. In contrast, we could observe additional long residuals in **1** and **3**, which most likely originate from the excited triplet state. Therefore, we can assume that the fast time components of **1** (3.5 ps) and **3** (2.0 ps) arise from the combination of the intersystem crossing from the singlet excited state to the triplet excited state and the relaxation of singlet excited state. In the Ni(II) porphycenes, we note a slight difference in the excited-state absorptions. As compared to the freebase porphycenes, the Ni(II)-derivatives show prominent excited state absorption bands at 700-750 nm (**Ni1**) and 600-650 nm (**Ni2** and **Ni3**). This particular feature most likely comes from the presence of a low-lying metal excited (d,d) state in Ni(II) complexes.[17] In **Ni2**, the two time components (1.5 ps and 85 ps) can be explained by the transition from the high-lying singlet exited-state to the low-lying metal excited (d,d) state followed by the relaxation from the (d,d) state to the singlet ground state. In analogy to **Ni2**, we can assume that the fast time component of 1.2 ps observed for **Ni1** and **Ni3** can be ascribed to the transition to the low-lying metal excited state, followed by the subsequent relaxation to the ground state with the time constants of 40 and 70 ps, respectively. In a similar fashion to **1** and **3**, the long residuals in **Ni1** and **Ni3** are associated with the excited triplet state.

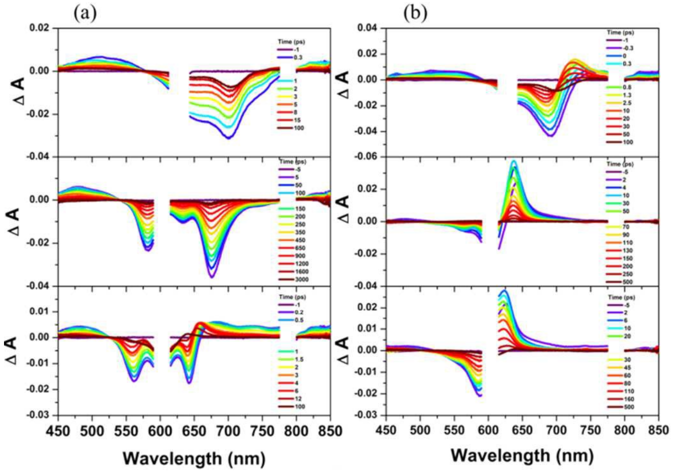


Fig. 4 TA spectra of (a) **1** (top), **2** (middle) and **3** (bottom), and (b) **Ni1** (top), **Ni2** (middle), and **Ni3** (bottom) in toluene obtained with photoexcitation at 630 nm (top), 600 nm (middle) and 600 nm (bottom), respectively.

The redox potentials of porphycene **1** and its metallo-derivatives were determined by cyclic voltammetry and differential pulse voltammetry techniques in dichloromethane using tetrabutylammonium hexafluorophosphate as the supporting electrolyte (Fig. S19-22 in the ESI† and Table 1). All porphycenes display the typical two reversible and/or quasi-reversible one-electron reductions and two reversible and/or quasi-reversible one-electron oxidations. Porphycene **1** shows the first reduction potential at -0.43 V and the first oxidation potential at +1.09 V, respectively, which are 0.68 and 0.31 V more positive compared to **3**, clearly revealing its more electron deficient nature.[7] Also, there is a drastic change in the first reduction potential compared to the first oxidation potential, upon introduction of electron withdrawing substituents, indicating greater stabilization of its LUMO. All metal complexes of porphycene **1** display two reversible oxidation and two reversible reduction potentials. Similar to the freebase porphycene **1,** an analogous trend was observed in oxidation and reduction potentials for **Zn1** and **Ni1** complexes compared to their corresponding octamethoxy analogues (Table 1).[7] The HOMO-LUMO gap (ΔE) for porphycene **1** is 1.52 V, which is

Table 1: Redox potentials (in V vs SCE) for porphycenes and their M(II) complexes

Porphycenes	Reduction	Oxidation	ΔE (V)
1	-0.54[a], -0.43[a]	+1.09[a], +1.25[a]	1.52
Zn1	-0.93[a], -0.68	+0.90[a], +0.98[a]	1.58
Ni1	-0.68[a], -0.55[a]	+1.01, +1.30	1.56
3[b]	-1.29, -1.11	+0.78, +1.15	1.89
Zn3[b]	-1.38, -1.13	+0.60, +0.75	1.73
Ni3[b]	-1.45, -1.19	+0.71, +1.17	1.90

[a] measured by DPV and [b] taken from ref 7.

0.37 V lower than **3**, and is in excellent agreement with the observed red shift in the low-energy band in the UV-Vis spectrum.[7] The ΔE for porphycene **1** is marginally higher (0.08 V) than that of porphycene **4,** which can be attributed to its smaller degree of distortion than **4**.[10]

Porphycene **1** could be further converted to the parent unsubstituted porphycene **8** (Scheme S1 in the ESI†), via deprotection using Raney Ni/H_2 at room temperature, followed by oxidation with DDQ, in 61% yield. Synthesis of this porphycene was initially reported by Vogel and coworkers, but suffers from a very poor yield.[1] Only recently, Waluk and coworkers have reported that the yield could be improved (65%) by deprotection of *tert*-butyl groups of 2,7,12,17-tetra-*tert*-butylporphycene upon heating at very high temperature (200 °C) under strong acidic condition.[18]

In conclusion, we have efficiently synthesized the first porphycene endowed with electron-deficient substituents at all *β*-positions, i.e. octa(methylthio)porphycene by employing oxidative coupling of 3,4-di(methylthio)pyrrole. With the current methodology using $BF_3.OEt_2$, we show that we can enhance the oxidative power of PIFA to synthesize electron deficient bipyrroles directly from their constituent pyrroles in a single step. The third order nonlinear optical studies of *β*-octasubstituted porphycenes and their Ni(II) complexes revealed that the modulation of substituents at the macrocyclic periphery affects their NLO response. Finally, owing to its mild deprotection ability, methylthio groups can be employed towards the synthesis of novel functionalized porphycenes, research in this direction is currently underway.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Detailed synthetic procedure, characterization, photophysical data and crystal data for **1** and **7** (CIF). CCDC No. 1052052 and 1052053. See DOI: 10.1039/c000000x/

1 E. Vogel, M. Kocher, H. Schmickler and J. Lex, *Angew. Chem. Int. Ed. Engl*., 1986, **25**, 257.

2 (a) J. C. Stockert, M. Cañete, A. Juarranz, A. Villanueva, R. W. Horobin, J. I. Borrell, J. Teixidó and S. Nonell, *Curr. Med. Chem*., 2007, **14**, 997; (b) D. Sánchez-García and J. L. Sessler, *Chem. Soc. Rev*., 2008, **37**, 215.

3 (a) T. Sarma, P. K. Panda, P. T. Anusha and S. V. Rao, *Org. Lett*., 2011, **13**, 188; (b) S. V. Rao, T. S. Prashant, D. Swine, T. Sarma, P. K. Panda and S. P. Tewari, *Chem. Phys. Lett*., 2011, **514**, 98; (c) J. Arnbjerg, A. Jiménez-Benzo, M. J. Paterson, S. Nonell, J. I. Borell, O. Christiansen and P. R. Ogilby, *J. Am. Chem. Soc*., 2007, **129**, 5188; (d) K. K. Kim, Y. M. Sung, T. Matsuo, T. Hayashi and D. Kim, *Chem. –Eur. J*., 2011, **17**, 7882.

4 D. Swain, A. Rana, P. K. Panda, S. V. Rao, *Chem. Phys. Lett*., 2014, **610-611**, 310.

5 (a) P. Thamyongkit, A. D. Bhise, M. Taniguchi and J. S. Lindsey, *J. Org. Chem*., 2006, **71**, 903; (b) M. R. Martinez-Gonzalez, A. Urías-Benavides, E. Alvarado-Martinez, J. C. Lopez, A. M. Gómez, M. d. Rio, I. Garcia, A. Costela, J. Bañuelos, T. Arbeloa; I. L. Arbeloa and E. Peña-Carbrera, *Eur. J. Org. Chem*., 2014, 5659; (c) F. Pan and Z.-J. Shi, *ACS Catal*., 2014, **4**, 280; (d) T. Higashino, M. S. Rodríguez-Morgade, A. Osuka and T. Torres, *Chem. –Eur. J*., 2013, **19**, 10353.

6 (a) E. Vogel, P. Koch, X.-L. Hou, J. Lex, M. Lausmann, M. Kisters, M. A. Aukauloo, P. Richard and R. Guilard, *Angew. Chem., Int. Ed. Engl*., 1993, **32**, 1600.

7 A. Rana and P. K. Panda, *Org. Lett*., 2014, **16**, 78.

8 (a) K.-i. Sugiura, M. R. Kumar, T. K. Chandrashekar and Y. Sakata, *Chem. Lett*., 1997, **26**, 291; (b) K. -i. Sugiura, K. Ushiroda, M. T. Johnson, J. S. Miller and Y. Sakata, *J. Mater. Chem*., 2000, **10**, 2507.

9 T. Dohi, K. Morimoto, A. Maruyama and Y. Kita, *Org. Lett*., 2006, **8**, 2007.

10 T. Hayashi, Y. Nakashima, K. Ito, T. Ikegami, I. Aritome, A. Suzuki and Y. Hisaeda, *Org. Lett*., 2003, **5**, 2845.

11 M. Stępień, B. Donnio and J. L. Sessler, *Chem. –Eur. J*., 2007, **13**, 6853.

12 (a) K. S. Kim, S. B. Noh, T. Katsuda, S. Ito, A. Osuka and D. Kim, *Chem. Commun*., 2007, **24**, 2479; (b) M. Albota, D. Beljonne, J.-L. Brédas, J. E. Ehrlich, J.-Y. Fu, A. A. Heikal, S. E. Hess, T. Kogej, M. D. Levin, S. E. Marder, D. McCord-Maughon, J. W. Perry, H. Röckel, M. Rumi, G. Subramaniam, W. W. Webb, X.-L. Wu and C. Xu, *Science*, 1998, **281**, 1653.

13 T. Tanaka, B. S. Lee, N. Aratani, M.-C. Yoon, D. Kim and A. Osuka, *Chem. –Eur. J*., 2011, **17**, 14400.

14 H. Mori, T. Tanaka, N. Aratani, B. S. Lee, P. Kim, D. Kim and A. Osuka, *Chem. –Asian J*., 2012, **7**, 1811.

15 Z. S. Yoon, J. H. Kwon, M.-C. Yoon, M. K. Koh, S. B. Noh, J. L. Sessler, J. T. Lee, D. Seidel, A. Aguilar, S. Shimizu, M. Suzuki, A. Osuka and D. Kim. *J. Am. Chem. Soc*., 2006, **128**, 14128.

16 (a) R. Andreu, M. J. Blesa, L. Carrasquer, J. Garín, J. Orduna, B. Villacampa, R. Alcalá, J. Casado, M. C. R. Delgado, L. Navarrete and M. Allain, *J. Am. Chem. Soc*., 2005, **127**, 8835; (b) T.-T. Bui, A. Iordache, Z. Chen, V. M. Roznyatovsky, E. Saint-Aman, J. M. Lim, B. S. Lee, S. Ghosh, J.-C. Moutet, J. L. Sessler, D. Kim and C. Bucher, *Chem. –Eur. J*., 2012, **18**, 5853; (c) H. Rath, V. Prabhuraja, T. K. Chandrashekar, A. Nag, D. Goswami and B. S. Joshi, *Org. Lett*., 2006, **8**, 2325.

17 H. S. Eom, S. C. Jeoung, D. Kim, J. -H. Ha and Y. R. Kim, *J. Phys. Chem. A*, 1997, **101**, 3661.

18 N. Urbańska, M. Pietraszkiewicz and J. Waluk, *J. Porphyrins Phthalocyanines*, 2007, **11**, 596.