



Synthesis and properties of C–C conjugated phthalocyanine dimers

Hasrat Ali, Pierre Baillargeon, Johan E. van Lier*

Department of Nuclear Medicine and Radiobiology, Faculty of Medicine and Health Sciences, Université de Sherbrooke 3001, 12th Avenue North, Sherbrooke, QC, Canada J1H 5N4

ARTICLE INFO

Article history:

Received 8 September 2008

Revised 25 September 2008

Accepted 26 September 2008

Available online 2 October 2008

ABSTRACT

Covalently C–C linked Pc–Pc homo-dimers (*ortho* and *meta*) were synthesized from their corresponding Pc halide precursors using a Pd-catalyzed homo-coupling reaction. Photophysical data reveal energy transfer between the Pc moieties resulting in the appearance of new red-shift Q-bands that correlate to the planarity and dihedral angle between the subunit.

© 2008 Elsevier Ltd. All rights reserved.

Phthalocyanines (Pcs) possess outstanding electronic properties including strong absorption in the visible region.¹ They have been extensively studied for applications in diverse fields such as medicine (photodynamic agents),² catalysis,³ biomimetic model systems for primary processes of natural photosynthesis,⁴ while Pc dyads attract attention for their use in opto-electric devices, super molecular assemblies, active components in semiconductors, electrochromic devices, information storage systems, and liquid crystal displays.⁵ In previously described conjugated and non-conjugated Pc dyads systems, different rigid or flexible spacer groups have been used to connect the two chromophores.⁶ Planar homo-dimers of Pc sharing benzene or naphthalene rings have also been published,⁷ however, directly C–C linked dimers have not been reported.

Reductive dimerization of aryl halides is one of the venerable methods for the preparation of symmetrical biaryl compounds. The most common way to prepare such compounds is the Ulmann synthesis.⁸ More recently, the preparation of biaryl compounds by Pd(0)-catalyzed cross-coupling reactions has also been reported.⁹ Monoiodo Pc had previously been used as building blocks for the syntheses of new mononuclear unsymmetrical Pc through a Pd-catalyzed coupling reaction.¹⁰ In this Letter, we report an efficient method for the synthesis of C–C linked Pc homo-dimers, connected directly between benzene rings, using Pd-catalyzed homo-coupling of monoiodo Pc. Their photophysical properties are explained by their computed dihedral angles.

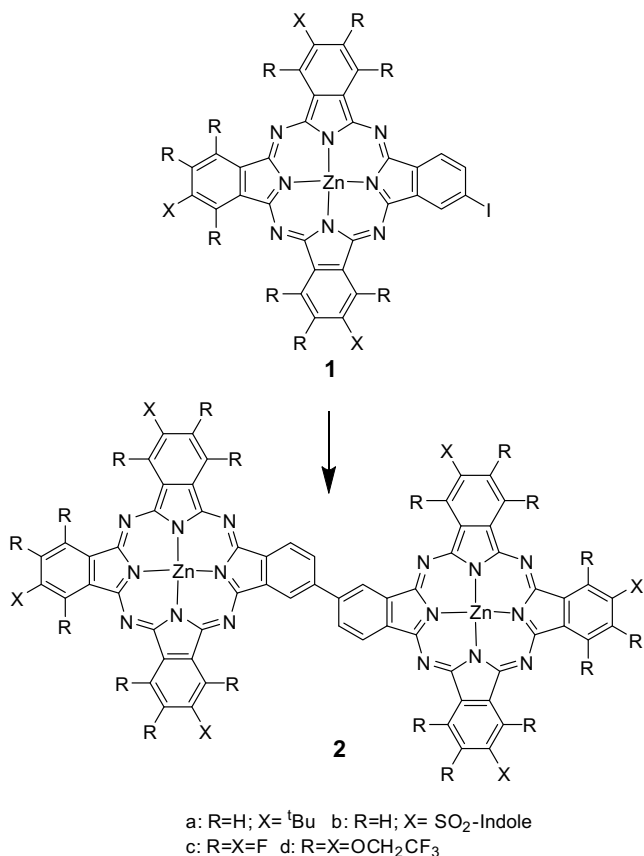
Using the Lemaire coupling method,⁹ monoiodo tri-*t*-butyl zinc phthalocyanine (**1a**) was treated with Pd(OAc)₂ and *n*-Bu₄NH₄Br in DMF/H₂O/K₂CO₃/isopropanol at 90 °C for 2 h. After purification, MS analysis revealed the presence of two products that could only be separated by reversed-phase C-18 chromatography in THF–H₂O. The major compound (60%) corresponds to the reduced Pc (MS-FAB 744.1; λ_{max} 671 nm), whereas the second compound (16%) corresponds to the Pc–Pc homo-coupled product (MS-FAB 1489.35;

100%). Changing the solvent system and the base decreased dimer yield. Aryl halides-catalyzed homo-coupling can be promoted by fluoride ions.¹¹ Thus, we treated compound **1a** with a 1 M solution of TBAF/THF in the presence of Pd(dba)₂ catalyst in toluene. After 2 h stirring at rt under argon, HPLC analysis revealed a 90% conversion to a mixture of 30% reduced Pc and 60% homo-coupled product (**2a**). Changing the catalyst to allyl palladium chloride dimer [Pd(π-allyl)Cl]₂ resulted in a slight increase in dimer formation (77%) after reacting for 24 h.¹²

Previously, we reported that base hydrolysis of imidazole-protected sulfonated Pc provides an alternate route to prepare water soluble Pc derivatives.¹³ We explored this route for the preparation of water soluble homo-coupled product. Thus, we treated 2-iodo-9,16,23(1'-indolylsulfonyl)ZnPc (**2b**) with Pd(OAc)₂ and *n*-Bu₄NH₄Br, isopropylethylamine in DMF at 90 °C for 2 h. The homo-coupled product **2b** was obtained in 20% yield (MS 2227.1; 100%). The homo-coupled products are regioisomers due to the parent monomers **1a** and **1b**. To obtain a single isomeric product, we selected a highly symmetrical F-substituted Pc monomer **1c** as precursor. Treatment of **1c** with Pd(OAc)₂, *n*-Bu₄NH₄Br in DMF/H₂O/K₂CO₃/isopropanol at 90 °C for 2 h provided a single isomer of homo-coupled **2c** (MS 1584.8). Products **2b,c** are highly aggregated in various organic solvents (absence of a sharp Q-band) rendering their separation from reduced Pc difficult. Substitution of monoiodo ZnPc with dodecakis(2,2,2-trifluoroethoxy) (**1d**) reduces the tendency to aggregate.¹⁴ We used **1d** for homo-coupling via treatment with Pd(OAc)₂, *n*-Bu₄NH₄Br, di-isopropylethylamine in toluene at 90 °C for 3 h to yield dimer **2d** in 50% yield along with 30% reduced Pc. The UV–vis spectrum of dimer **2d** gave a single Q-band at λ_{max} 704 nm and MALDI-TOF MS molecular ion at 3505.1 (100%) (Scheme 1).

To compare the effect of *meta* versus *ortho* coupling on their photophysical properties, we also prepared homo-coupled dimer linked at the *ortho*-position of the benzene ring. Treatment of **3** with allyl Pd dimer catalyst and 2-di-*t*-butylbiphenyl ligand using the optimal procedure as developed for compound **2a**, surprisingly failed to give homo-coupled product and mostly reduced Pc was

* Corresponding author. Tel.: +1 819 564 5409; fax: +1 819 564 5442.
E-mail address: johan.e.vanlier@usherbrooke.ca (J. E. van Lier).



Scheme 1.

detected. Instead the homo-coupled product **4** was obtained using *n*-Bu₄NH₄Br with (Pd)₂(dba)₃ (10–15% yield) or Pd(OAc)₂ and isopropylethylamine in DMF at 90 °C for 2 h (15–20% yield). The low yield likely reflects steric hindrance between the two subunits, favoring formation of the reduced Pc (Scheme 2).

The optical features of the binuclear chromophoric system in THF differ significantly from those of the corresponding parent monomer (Fig. 1). Pc **1a** shows a sharp Q-band at 672 nm, while binuclear *meta*-coupled **2a** shows two Q-bands of similar intensity; one at 671 nm corresponding to the absorption maximum of the monomer and a second bathochromic shifted band at 703 nm. The electronic absorption spectrum of the *ortho*-coupled homo-dimer **4** likewise shows two Q-bands; one at 668 nm and a second,

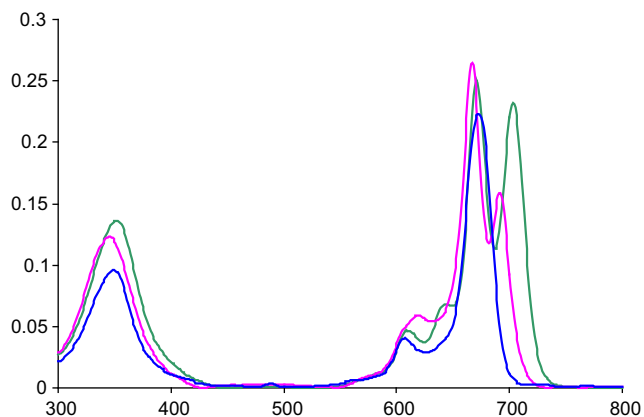


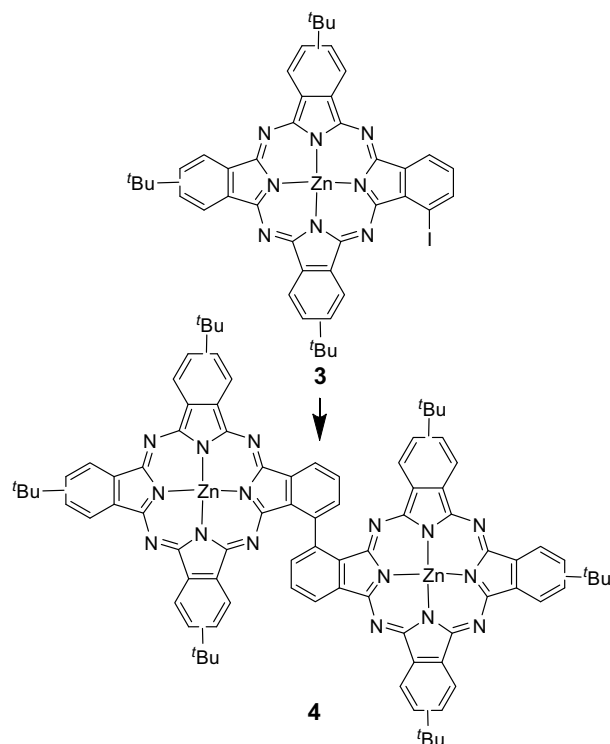
Figure 1. Electronic spectra of ZnPc(*t*-Bu)₄ (**1a**) (blue) and the *ortho*-coupled dimer **3** (red) and *meta*-coupled dimer **2a** (green).

less intense band at 691 nm. The new red-shifted Q-bands can be attributed to the enlargement of the π -conjugated system due to intramolecular electronic coupling between the two subunits of the homo-coupled dimers.

The less prominent bathochromic shift of the split Q-band observed with the *ortho*-coupled dimer **3**, as compared to that observed with the *meta*-analog **2a**, as well as the lower intensity of the former, likely reflects differences in the planarity of the two homo-coupled products. The calculated C–C bond length, that is, edge-to-edge distances between the two Pc subunits of the dimers corresponds to 1.5025 Å (**2a**) and 1.464 Å (**3**). This close distance between the subunits allows for strong excitonic coupling. The computed minimum energy conformation for the *meta*-coupled dimer **2a** predicts a 31.1° dihedral angle between the Pc rings (Fig. 2), which is a little bit lower than that of the known biphenyl system.¹⁵ This relatively planar geometry conformation suggests that a certain degree of π -conjugation is allowed between the two Pc subunits; the twisted conformer being the best compromise between resonance stabilization and steric repulsions. On the other hand, the *ortho*-dimer **4** (Fig. 2) adopts a nearly perpendicular orientation (dihedral angle = 101.6°). The planar conformation is not allowed in this case due to serious sterical hindrance, and as a consequence the degree of π -conjugation is lower as that obtained with the *meta*-dimer **2a**.

Interestingly, in the case of the trifluoroethoxy-coated binuclear Pc **2d**, we found that the red shift of the Q-band is not as prominent as that observed with the *t*-Bu analog **2a**. Furthermore, the Q-band of **2d** is not split in most solvents tested, only in DMF a small doublet was observed (Fig. 3). These observations are in agreement with recently published spectral properties of a butadiynyl-bridged trifluoroethoxy-coated Pc dimer, where no Q-band splitting was observed.¹⁷

In summary, novel covalently C–C linked Pc–Pc homo-dimers (*ortho* and *meta*) were prepared from their corresponding Pc halide precursors using a Pd-catalyzed homo-coupling reaction. Photo-physical data reveal energy transfer between the Pc moieties



Scheme 2.

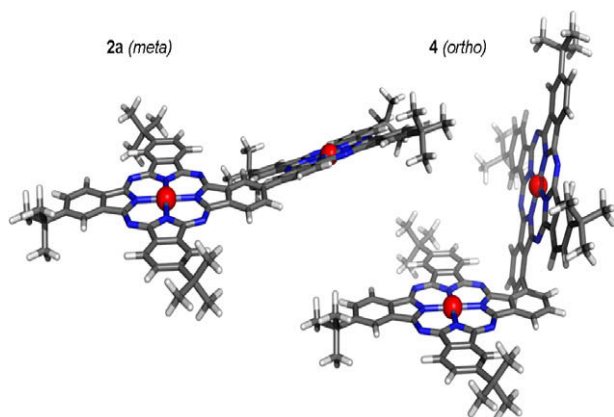


Figure 2. Minimum energy conformations of ZnPc-dimers obtained from DFT computations (B3LYP/SBKJC). Software: GAMESS.¹⁶

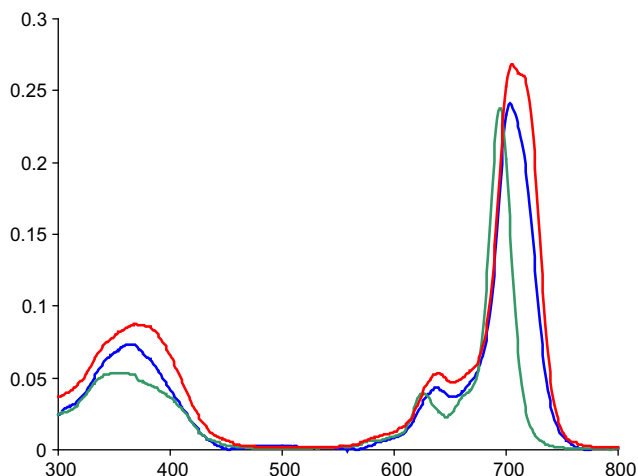


Figure 3. Electronic spectra of ZnPc(OCH₂CF₃)₁₂ (**1d**) (green) and the ortho-coupled dimer **2d** in THF (blue) and DMF (green).

resulting in the appearance of new red-shift Q-bands. The intensity and extent of the bathochromic shift correlate with the planarity and dihedral angle between the subunits.

Acknowledgment

Supported by the Jeanne and J.-Louis Lévesque Chair in Radiobiology of the Université de Sherbrooke.

References

- (a) *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: San Diego, CA, 2003; (b) *Phthalocyanines Materials: Synthesis Structure and Function*; McKeown, N. M., Ed.; Cambridge University Press: Cambridge, 1998; (c) de la Torre, G. M.; Nicolau, M.; Torres, T. In *Supramolecular Photosensitive and Electroactive Materials*; Nalwa, H., Ed.; Academic Press: New York, 2001; p 1; (d) *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; Wiley-VCH: Weinheim, Germany, 1989, Vols. 1–4.
- (a) Ali, H.; van Lier, J. E. *Chem. Rev.* **1999**, *99*, 2379–2450; (b) Sharman, W. M.; Allen, C. M.; van Lier, J. E. *J. Porphyrins Phthalocyanines* **2001**, *5*, 161–169; (c) Sharman, W. M.; Allen, C. M.; van Lier, J. E. *Drug Discovery Today* **1999**, *4*, 507–517.
- Tao, X.; Ma, W.; Zhang, T.; Zhao, J. *Chem. Eur. J.* **2002**, *8*, 1321–1326.
- Satake, A.; Kobuke, Y. *Org. Biomol. Chem.* **2007**, *5*, 1579–1691.
- de la Torre, G. M.; Claessen, C. G.; Torres, T. *Chem. Commun.* **2007**, 2000–2015.
- (a) Nevin, W. A.; Hempstead, W. L.; Leznoff, C. C.; Lever, A. B. P. *Inorg. Chem.* **1987**, *26*, 570–577; (b) Leznoff, C. C.; Lam, H.; Nevin, W. A.; Kobayashi, N.; Janda, P.; Lever, A. B. P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1021–1023; (c) Lyubimtsev, A.; Iqbal, Z.; Hanack, M. *Aust. J. Chem.* **2008**, *61*, 273–278; (d) Aysegül, Y.; Davut, A.; Ozer, B.; Nagao, K. *J. Porphyrins Phthalocyanines* **2006**, *10*, 1140–1144; (e) Jimenez, A. J.; Spanig, F.; Rodriguez-Morgade, M. S.; Ohkubo, K.; Fukuzumi, S.; Guldi, D. M.; Torres, T. *Org. Lett.* **2007**, *9*, 2481–2488; (f) Leznoff, C. C. *Can. J. Chem.* **2000**, *78*, 167–183.
- (a) Cook, M.; Heeney, M. *J. Chem. Eur. J.* **2000**, *6*, 3958–3967; (b) Maya, E. M.; Vazquez, P.; Torres, T.; Gobbi, D. F.; Pyo, S.; Echegoyen, L. *J. Org. Chem.* **2000**, *65*, 823–830; (c) Maya, E. M.; Vazquez, P.; Torres, T. *Eur. J. Chem.* **1999**, *5*, 2004–2013; (d) Quintiliani, M.; Garcia-Frutos, E. M.; Vazquez, P.; Torres, T. *J. Inorg. Biochem.* **2008**, *102*, 388–394.
- (a) Ulmann, F. *Ber.* **1903**, *36*, 2389; (b) Fanta, E. *Synthesis* **1974**, *1*, 9–21.
- (a) Hassan, J.; Hathroubi, C.; Gozzi, C.; Lemaire, M. *Tetrahedron* **2001**, *57*, 7845–7855; (b) Hassan, J.; Hathroubi, C.; Gozzi, C.; Lemaire, M. *Tetrahedron Lett.* **2000**, *40*, 8791–8794; (c) Albanese, D.; Landini, D.; Penso, M.; Petricci, S. *Synlett* **1999**, 199–200.
- (a) Ali, H.; van Lier, J. E. *Tetrahedron Lett.* **1997**, *38*, 1157–1160; (b) Martinez-Diaz, M. V.; Quintiliani, M.; Torres, T. *Synlett* **2008**, 1–20; (c) Sharman, W. M.; van Lier, J. E. *J. Porphyrins Phthalocyanines* **2000**, *4*, 441–4453.
- Seganish, W. M.; Mowery, M. E.; Riggelman, S.; DeShong, P. *Tetrahedron* **2005**, *61*, 2117–2121.
- Denmark, S. E.; Ober, H. M. *Org. Lett.* **2003**, *5*, 1357–1360.
- Tian, H.; Ali, H.; van Lier, J. E. *Tetrahedron Lett.* **2000**, *41*, 8435–8438.
- Tian, M.; Wada, T.; Sasabe, H. *J. Heterocycl. Chem.* **2000**, *37*, 1193–1201.
- Göller, A.; Grummt, U.-W. *Chem. Phys. Lett.* **2000**, *321*, 399–405.
- Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsuraga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347–1363.
- Yoshiyama, H.; Shibata, N.; Sato, T.; Nakamura, S.; Toru, T. *Chem. Commun.* **2008**, 1977–1979.