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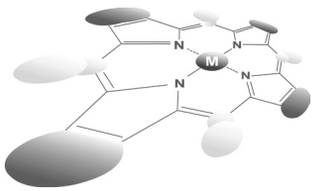

Synthesis of symmetrical and unsymmetrical subphthalocyanine dimers containing a hydroquinone bridge

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ABSTRACT: Three novel hydroquinone-based symmetrically and unsymmetrically substituted subphthalocyanine (SubPc) dimers have been synthesized through the axial substitution of the macrocycle. The mono SubPc hydroquinone derivative (Hq-SubPc) first prepared acts as a nucleophile which replaces the chlorine atom of the second SubPc molecule to form the dimer. The dimers were obtained by reacting hydroquinone and the respective SubPcs in a 1:1 molar ratio in toluene at 180 °C in a pressure vessel. This new approach allowed stoichiometric quantities of reactants to be utilized. All dimers were characterized by ^{1}H NMR, ^{13}C NMR, UV-vis, fluorescence and mass spectral analysis.

KEYWORDS: subphthalocyanines, synthesis, NMR, UV-vis, fluorescence, mass spectra.

INTRODUCTION

In the last few years interest in phthalocyanines (Pc) and metallophthalocyanines has risen because of their diverse technological applications in various fields of materials science [1]. This stimulated the preparation of a few phthalocyanine (Pc) homologs such as metal incorporated phthalocyanines, extended π-systems *via* modifying the phthalocyanine ring, and systems with a variety of isoindole units. Special examples of the Pc-related compounds are the so-called subphthalocyanines [2]. These are unique, ring-reduced members of Pc comprised of 14 π-electrons and three N-fused diiminoisoindole units around a boron atom [3]. The cone-shaped structure, the synthetic versatility [4], and the electron-accepting nature of the subphthalocyanines afford attractive photophysical and photochemical properties [5] as compared to the flat phthalocyanines. SubPcs have found applications in various fields *viz*., nonlinear optics, LEDs, photovoltaics, photodynamic therapy [6] and also in the study of energy- and electron-transfer processes [7]. In addition, the properties of the SubPcs can also be fine-tuned as their axial positions can be easily functionalized and derivatized [8]. These compounds have also proved to be of synthetic interest in terms of a ring expansion reactions to serve as precursors for the synthesis of unsymmetrically substituted phthalocyanines [9]. However, the physical properties of various substituted SubPcs have not been completely manipulated because of the complications involved in their synthesis and purification [8, 10]. To date, only a few subphthalocyanine derivatives have been reported through different synthetic pathways involving the peripheral and axial approaches [11]. The axial substitution of the SubPcs is advantageous in some respects, especially since the electronic structure of the SubPc is preserved. Certain chloro-subphthalocyanines (Cl-SubPcs) reacted with different phenols and gave interesting derivatives. Simple phenols offer a variety of derivatives, are available for facile introduction of new functional groups at the axial position of SubPcs, and allow the geometry of the adducts formed with SubPcs to be controlled by modulating the substitution pattern [12]. A few subphthalocyanine dimers (Fig. 1) in which the two macrocycles were in close proximity have been recorded [13]. We report for the first time the synthesis (Scheme 1) and spectroscopic characterization of three novel symmetrical and unsymmetrical dimers that are linked by a hydroquinone moiety and potentially offer enhanced electron distribution over the entire system.

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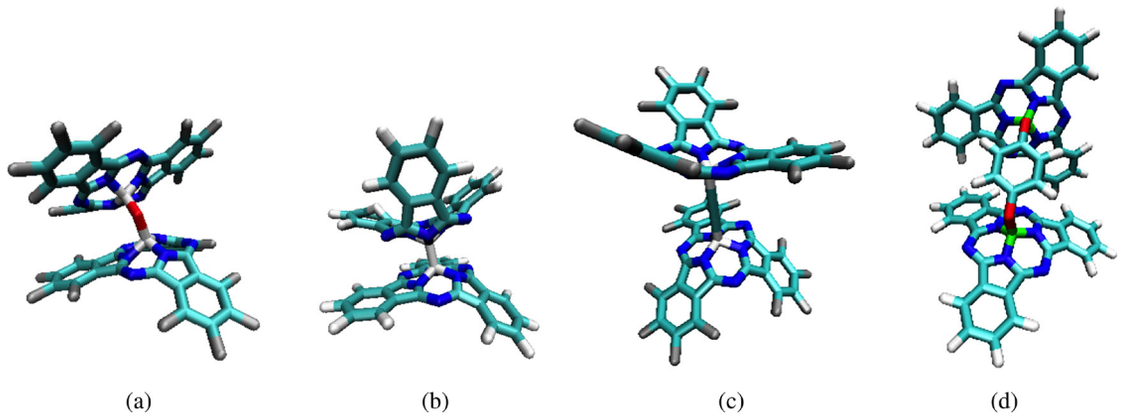
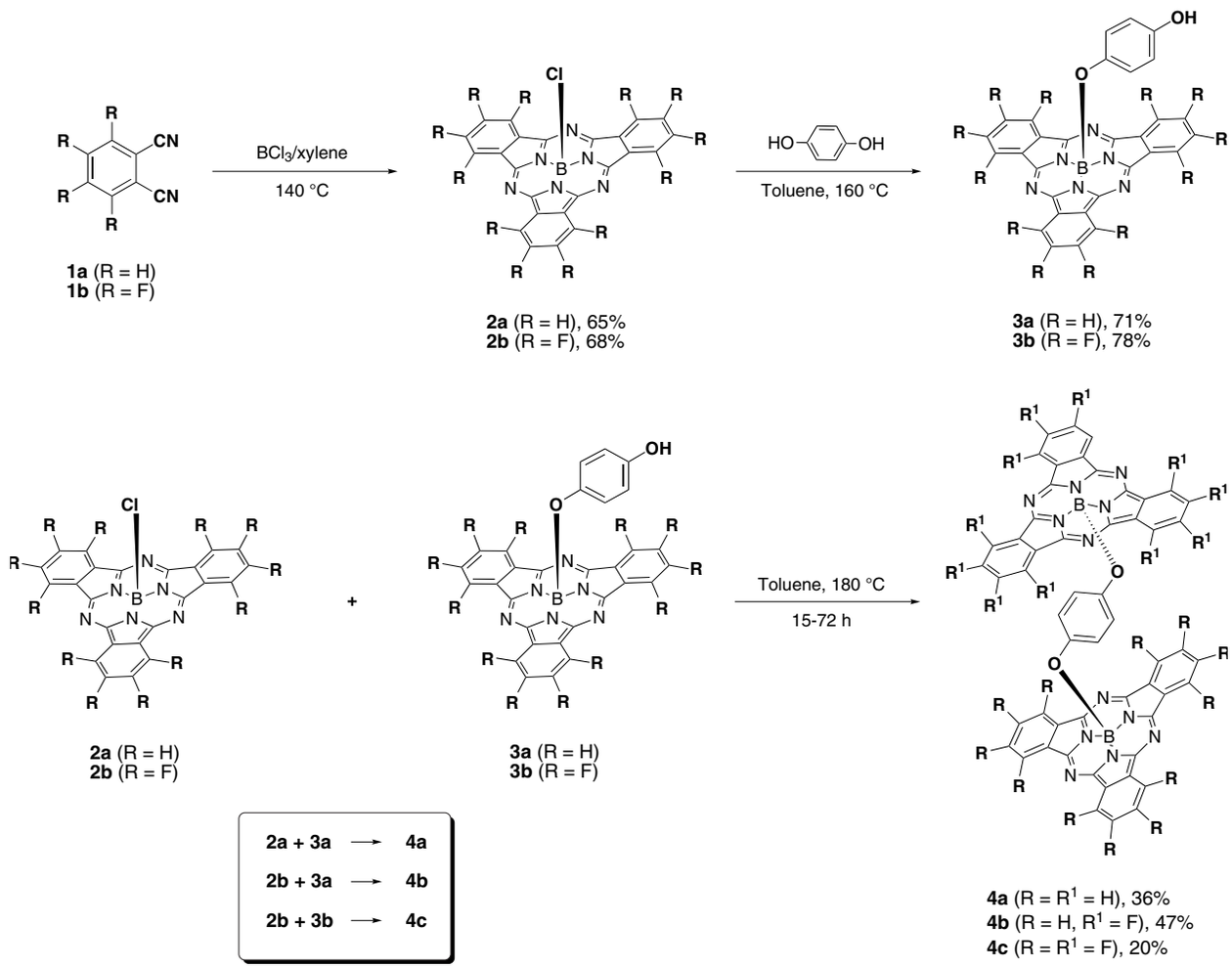


Fig. 1. Tubular representation of SubPc dimers (a) B–B bond (b) B–O bond (c) B–C–C–B bond and (d) B–Hq–B bond



Scheme 1. Synthesis of subphthalocyanine dimers

RESULTS AND DISCUSSION

Synthesis

The synthetic pathway to the dimers is shown in Scheme 1. The synthesis involved the cyclotrimerization of the phthalonitriles with BCl_3 (1 M solution in *p*-xylene) to give the parent Cl-SubPcs, **2a** and **2b**. This was then followed by the axial replacement of the chlorine atom in **2a** and **2b** by hydroquinone to generate the electron rich, hydroquinone-substituted Hq-SubPcs, **3a** and **3b**, respectively. The final step is the nucleophilic attack of

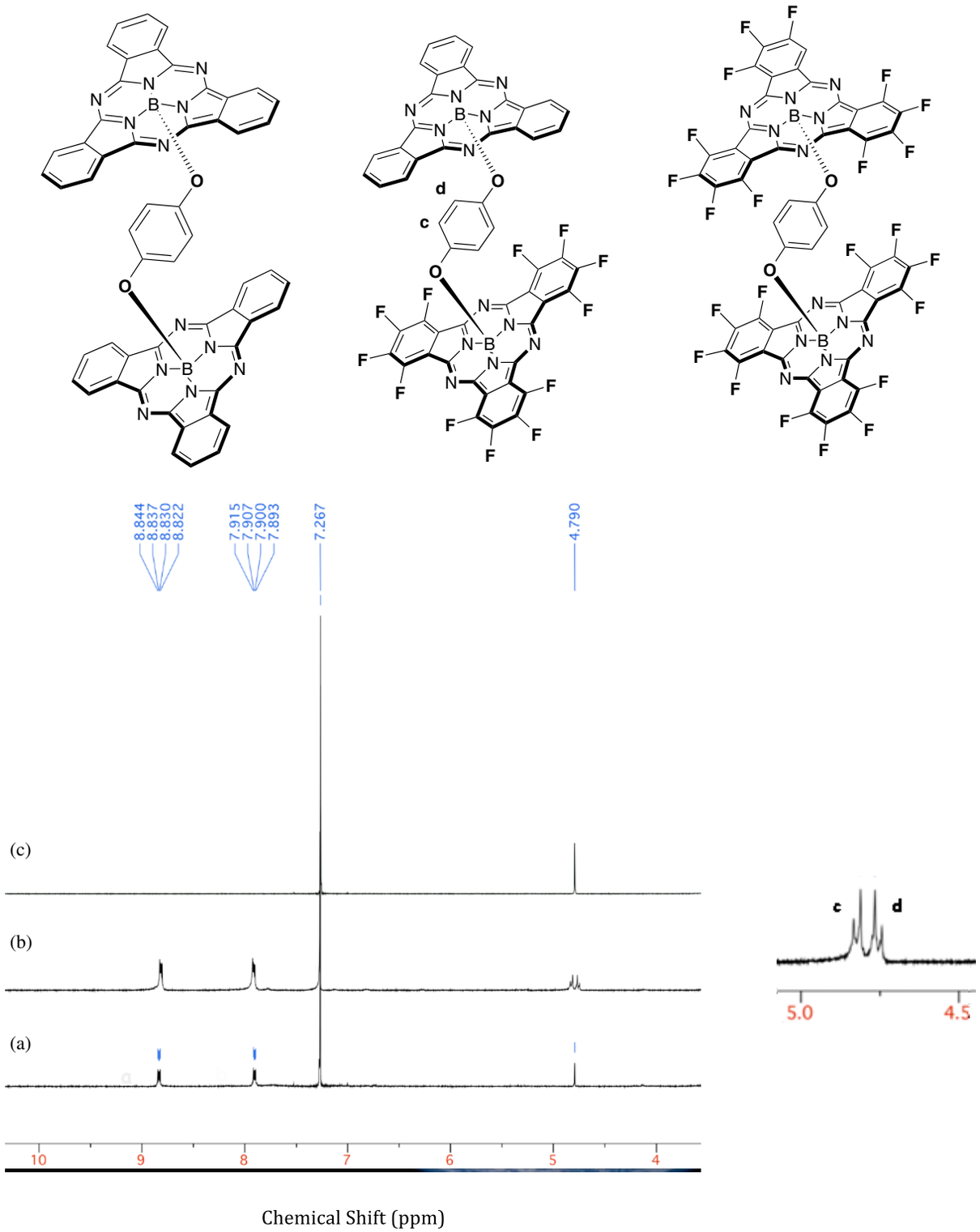


Fig. 2. ^{1}H NMR (400 MHz; $CDCl_3$; 299 K) of the dimers (a) $SubPc_{(H)}$-Hq-$SubPc_{(H)}$ (b) $SubPc_{(H)}$-Hq-$SubPc_{(F)}$ (c) $SubPc_{(F)}$-Hq-$SubPc_{(F)}$ and (d) expanded ^{1}H NMR spectrum of $SubPc_{(H)}$-Hq-$SubPc_{(F)}$

Hq-SubPcs **3a** and **3b** at the electropositive boron atom of **2a** and **2b** to give symmetrical and unsymmetrical dimers, **4a**, **4b** and **4c**.

Synthesis of Cl-SubPcs, 2a and 2b. Since **2a** and **2b** were key starting materials and were not commercial, both were synthesized from the corresponding phthalonitriles by modifying a somewhat general procedure pionered by Torres and co-workers [14]. Condensation of the phthalonitriles with 1 M solution of BCl_3 in *p*-xylene under argon at reflux conditions for 20–30 min afforded

2a and **2b** in yields comparable to those reported [14]. Easy handling and high boiling *p*-xylene made it an excellent solvent for the initial phthalonitriles [15]. Extraction (toluene) of the crude material, followed by drying, filtration and evaporation, yielded Cl-SubPcs which were chromatographed to give pure materials used directly in the next step.

Synthesis of Hq-SubPcs, 3a and 3b. Only a few phenoxy substituents have been used to replace the axial chlorine atom [16]. Solvent, reaction temperature, the nature of the phenolic substituent, and the electronic characteristics of the Cl-SubPcs appear to play leading roles in determining the yields obtained and the reaction time required. In general, with the use of a polar solvent, such as acetonitrile, the reaction appears to proceed faster but only with an average yield, presumably resulting from decomposition of the SubPcs in the polar media [17].

In an effort to increase the efficiency for the conversion of **2a** and **2b** to intermediates **3a** and **3b**, respectively, we attempted to employ a 1:1 ratio of **2a** with hydroquinone in dry toluene in a pressure vessel. A prior method utilized a 1:5 ratio of such reagents in regular lab glassware [18]. In our hands, the reaction in a pressure vessel in boiling toluene gave only moderate yields. However, heating the mixture to 160 °C for 10 h gave a comparable yield of **3a** to that reported [18]. Purification of our crude product *via* chromatography was straightforward for **3a** and for **3b**, the latter being obtained in a similar fashion but with only 1 h of reaction time. It is conceivable that the presence of the electronegative fluorine atoms in **2b** increased the electron deficiency of the boron atom which facilitated the nucleophilic attack.

Synthesis of SubPc-Hq-SubPc dimers, 4a–4c. Regarding the synthesis of the SubPc-hydroquinone dimers, various alterations were made on the reaction conditions. Since a few of the SubPcs previously reported were found to decompose with the addition of bases, such as NaH and DBU [14], the parameters that can be altered were solvent and the temperature. Reacting a 1:1 mixture of **2a** and **3a** in a high boiling solvent, namely *o*-dichlorobenzene under reflux conditions, had no effect on the reaction.

Next, we attempted the reaction of **2a** with **3a** in toluene at 180 °C using a pressure vessel. Thus, it was possible to isolate dimer **4a** (36%) in three days. No improvement in yield was observed with longer reaction times, but rather decomposition occurred. Dilution of the reaction mixture reduced the rate of the reaction. The crude product was directly chromatographed over silica gel using ethyl acetate:hexane (1:5) to give **4a**.

With the intent to synthesize the unsymmetrical dimer, it was assumed that **3a** would be a better nucleophile for **2b** due to the comparatively electropositive boron atom present in the latter. As expected, the reaction of **3a** with **2b** proceeded smoothly to give **4b** in a yield of 47% after purification by column chromatography using CH_2Cl_2:hexane (1:4). The symmetrical SubPc dimer **4c** was synthesized from reaction of **2b** with **3b** under similar conditions, but the yield was modest (20%), presumably because **3b** was a poor nucleophile. Mostly starting material was recovered.

Characterization and spectral properties

All intermediates and target dimers were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. As a result of the diamagnetic ring currents from the two SubPc units in the dimer, the ^{1}H NMR resonances of the linking hydroquinone moiety showed considerable upfield shifts. For the symmetrical dimers **4a** and **4c** all the protons experienced the same environment with a sharp singlet at 4.79 ppm, corresponding to protons of the hydroquinone bridge. In contrast, for the unsymmetrical dimer **4b**, as expected, two different proton signals appeared as two doublets between 4.83–4.73 ppm (Fig. 2). These compounds are the first examples of subphthalocyanine dimers where the spacer hydroquinone moiety bridged the two systems. This was validated by a high upfield shift of the aromatic protons to 4.7 ppm compared to proton signals (6.21 and 5.20 ppm) on a previously reported, single phenolic linker [18].

The UV-vis experiments showed three distinct absorption curves for the SubPc dimers with λ_{max} = 562, 566, 572 nm for **4a**, **4b** and **4c**, respectively. The fluorinated dimer **4c**, showed a considerable red shift of about 10 nm from the unsubstituted dimer, **4a**. As expected, the λ_{max} for the unsymmetrically substituted SubPc dimer **4b** was found between the 562–572 nm range, which suggests that the absorption maximum of the dimers can be accordingly tailored by incorporating SubPcs containing different peripheral groups.

EXPERIMENTAL

General

Melting points (mp) were determined using a Stuart SMP10 instrument. Both ^{1}H and ^{13}C NMR spectra were acquired in $CDCl_3$ using a Varian Inova 400 MHz spectrometer. Chemical shifts (δ) are expressed in ppm relative to residual chloroform (^{1}H: 7.26 ppm, ^{13}C: 77.0 ppm) or to TMS. Fourier Transform Infrared (FT-IR) measurements were performed on a Varian 800 FT-IR spectrometer. UV-vis spectra were recorded on a Cary 5000 UV-vis-NIR spectrophotometer. Fluorescence spectra were recorded on a Cary Eclipse fluorescence spectrophotometer. All UV-vis and fluorescence spectra were recorded [1.0×10^{-7} M] at 23 °C. Chromatography was carried out on silica gel (Sorbent Technologies, 230–400 mesh). All compounds were pure by TLC which was done with polyester sheets precoated with silica gel (Sorbent Technologies). Phthalonitrile (Alfa Aeser), tetrafluorophthalonitrile, BCl_3 (Sigma Aldrich)

and hydroquinone (Fischer) were purchased from commercial suppliers and used as received unless otherwise indicated.

Synthesis

Standard procedure A for the synthesis of SubPcs (2a and **2b).** To a 100-mL, two-necked, round-bottomed flask fitted with a condenser, magnetic stirrer and septum, was added the corresponding dry phthalonitrile (2 mmol), under argon, followed by dropwise addition of BCl_3 (2 mL, 1 M solution in *p*-xylene) at room temperature. The mixture was refluxed for 30 min to yield a purple solution. The system was flushed with argon for 15 min. The solvent was evaporated, and the solid obtained was extracted with toluene (1 × 20 mL), washed with brine (1 × 20 mL), dried (Na_2SO_4) and evaporated to yield slightly crude SubPcs which were further purified by chromatography over silica gel.

Standard procedure B for the axial substitution of SubPcs with hydroquinone (Hq-SubPc) (3a and **3b).** A mixture of Cl-SubPc (1.0 equiv.) and hydroquinone (1:5 equiv.) was refluxed in dry toluene in a 100-mL, single-necked, round-bottomed flask fitted with a condenser for 1–10 h. The reaction mixture was allowed to cool to room temperature, the solvent was evaporated, and the crude material was purified by column chromatography over silica gel using ethyl acetate:hexane in various ratios (1:3 to 1:5). When the ratio of 1:1 equivalents of starting materials was employed, a pressure vessel (CG-1880 Pressure Vessel from CHEMGLAS) was utilized.

Standard procedure C for the synthesis of SubPc dimers (4a–4c). The starting Cl-SubPc (1.0 equiv.), SubPc hydroquinone derivative, Hq-SubPc (1.0 equiv.), and dry toluene were placed in a pressure vessel and heated at 180 °C for 15–72 h. The solvent was evaporated, and the crude material was subject to column chromatography on silica gel using ethyl acetate:hexane or CH_2Cl_2:hexane in varying ratios to afford the dimers.

Cl-SubPc 2a. Phthalonitrile **1a** (0.5 g, 3.9 mmol) and BCl_3 (4 mL, 1 M solution in *p*-xylene) were allowed to react *via* procedure A. The solvent was evaporated, the solid was extracted in toluene (1 × 20 mL), and the organic layer was washed with brine (1 × 20 mL), dried (Na_2SO_4), and evaporated to afford **2a** (1.34 g, 80%); mp > 300 °C (lit[14] mp > 250 °C; yield 82%). Our purified chromatographed product (65%) had the same mp.

Cl-SubPc 2b. Tetrafluorophthalonitrile **1b** (0.5 g, 2.5 mmol) and BCl_3 (4 mL, 1 M solution in *p*-xylene) reacted *via* procedure A. The solvent was evaporated, the solid was extracted in toluene (1 × 20 mL), and the organic layer was washed with brine (1 × 20 mL), dried (Na_2SO_4), and evaporated to afford **2b** (1.41 g, 88%); mp > 300 °C (lit[14] mp > 250 °C; yield 74%). Our purified chromatographed product (68%) had the same mp.

Hq-SubPc 3a. The starting Cl-SubPc **2a** (0.4 g, 0.9 mmol) and hydroquinone (0.1 g, 0.9 mmol) were heated to 160 °C in dry toluene (5 mL) for 10 h according to procedure B (pressure vessel). After cooling to rt, the reaction mixture was evaporated to dryness and chromatographed over silica gel using ethyl acetate:hexane (1:3) to afford **3a**, (0.33 g, 71%); mp > 300 °C (lit[18] mp > 250 °C; yield 80%). UV-vis (toluene): λ_{max}, nm 562 (Q-band). Fluorescence (λ_{exc} = 562 nm): λ_{em}, nm 573 (UV-vis and fluorescence studies were not reported in the literature previously).

Hq-SubPc 3b. The starting Cl-SubPc **2b** (0.2 g, 0.31 mmol) and hydroquinone (0.17 g, 1.5 mmol) were refluxed in dry toluene (3 mL) for 1 h according to procedure B (pressure vessel). The reaction mixture was evaporated to dryness, and the residue was chromatographed over silica gel using ethyl acetate:hexane (1:5) to afford **3b**, (0.17 g, 78%); mp > 300 °C (lit[18] mp > 250 °C; yield 61%). UV-vis (toluene): λ_{max}, nm 572 (Q-band). Fluorescence (λ_{exc} = 572 nm): λ_{em}, nm 586 (UV-vis and fluorescence studies were not reported in the literature previously).

$SubPc_{(H)}$-Hq-$SubPc_{(H)}$ dimer 4a. A mixture of Cl-$SubPc_{(H)}$, **2a** (50 mg, 0.1 mmol) and Hq-$SubPc_{(H)}$ **3a** (55.4 mg, 0.1 mmol) in dry toluene (2 mL) was treated according to procedure C for three days. Purification by column chromatography on silica gel using ethyl acetate:hexane (1:5) afforded **4a** (37.5 mg, 36%); mp > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 8.84–8.82 (AA′BB′, 6H, SubPc), 7.91–7.89 (AA′BB′, 6H, SubPc), 4.79 (s, 2H, Hq). ^{13}C NMR (300 MHz, $CDCl_3$): δ, ppm 151.0, 145.2, 130.8, 129.7, 122.3, 119.5. IR (CH_2Cl_2): ν, cm^{-1} 3023, 2922, 2855, 1697, 1651, 1497, 1457, 1376, 1288, 1217, 1132, 1054 (B–O bond), 738, 698. UV-vis (toluene): λ_{max}, nm 562 (Q-band). Fluorescence (λ_{exc} = 562 nm): λ_{em}, nm 573. MS-MALDI-TOF: *m/z* $C_{54}H_{28}B_2N_{12}O_2$, calcd. av. mass 899.26; obsd. 899.27 $[M]^+$.

$SubPc_{(H)}$-Hq-$SubPc_{(F)}$ dimer 4b. A mixture of Cl-$SubPc_{(F)}$, **2b** (25 mg, 0.038 mmol), and Hq-$SubPc_{(H)}$ **3a** (19.53 mg, 0.038 mmol) in dry toluene (1 mL) was treated according to procedure C for 15 h. The crude product was subjected to column chromatography on silica gel using CH_2Cl_2:hexane (1:4) to yield **4c** (20 mg, 47%); mp > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 8.84–8.82 (AA′BB′, 6H, SubPc), 7.91–7.89 (AA′BB′, 6H, SubPc), 4.73–4.83 (d, 2H, Hq). ^{13}C NMR (100 MHz, $CDCl_3$): δ, ppm 148.2, 145.9, 144.0(m), 141.3(m), 119.1, 114.7(m). IR (CH_2Cl_2): ν, cm^{-1} 3054, 2989, 1422, 1264, 1054 (B–O bond), 896, 778, 739, 699. UV-vis (toluene): λ_{max}, nm 566 (Q-band). Fluorescence (λ_{exc} = 566 nm): λ_{em}, nm 585. MS-MALDI-TOF: *m/z* $C_{54}H_{16}B_2F_{12}N_{12}O_2$, calcd. av. mass 1115.15; obsd. 1115.15 $[M]^+$.

$SubPc_{(F)}$-Hq-$SubPc_{(F)}$ dimer 4c. A mixture of Cl-$SubPc_{(F)}$, **2b** (50 mg, 0.07 mmol), and Hq-$SubPc_{(F)}$ **3b** (55.8 mg, 0.07 mmol) in dry toluene (2 mL) was treated according to procedure C. Purification by column chromatography on silica gel using ethyl acetate:hexane (1:7) afforded **4b** (20 mg, 20%); mp > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 4.79 (s, 2H). ^{13}C NMR

(300 MHz, $CDCl_3$): δ, ppm 148.3, 146.0, 144.1, 141.4, 119.3, 114.8. IR (CH_2Cl_2): ν, cm^{-1} 3058, 2930, 1780, 1743, 1486, 1265, 1055 (B–O bond), 116, 967, 779, 739, 698. UV-vis (toluene): λ_{max}, nm 572 (Q-band). Fluorescence (λ_{exc} = 572 nm): λ_{em}, nm 584. MS-MALDI-TOF: *m/z* $C_{54}H_4B_2F_{24}N_{12}O_2$, calcd. av. mass 1331.04; obsd. 1331.04 $[M]^+$.

CONCLUSION

In summary, we have synthesized three new hydroquinone-based, subphthalocyanine dimers, **4a**, **4b** and **4c** utilizing a 1:1 ratio of the ligand *vs.* SubPc in a pressure vessel at 180 °C. The use of a pressure vessel to prepare **3a**, **3b**, **4a**, **4b** and **4c** offers a major advantage in terms of minimizing the ratios of reactants. All structures were characterized using ^{1}H NMR and ^{13}C NMR spectroscopy. The hydroquinone bridge in the dimers showed characteristic upfield shifted aromatic protons because of the diamagnetic ring current of the two axial, covalently-linked SubPcs. In comparison to the symmetrical dimers **4a** and **4c**, the synthesis of the unsymmetrical dimer **4b**, obtained by reacting **3a** with **2b**, proceeded at higher yield (47%) and required a shorter reaction time (15 h). This is attributed to the increased axial reactivity of **2b**. The nucleophilicity of **3a** towards another SubPc molecule suggested the potential usefulness of such compounds as building blocks for the construction of higher order molecular assemblies. Furthermore, the new dimers possess improved solubility, compared to the systems with one hydroxyl phenolic linker [18], and may be of value in several thin film applications in optoelectronic devices.

Acknowledgements

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Supporting information

Figures S1–S5 are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

REFERENCES

1. de la Torre G, Claessens CG and Torres T. *Chem. Commun*. 2007; 2000–2015.
2. a) Torres T. *Angew. Chem. Int. Ed.* 2006; **45**: 2834. b) Claessens CG, González-Rodríguez D and Torres T. *Chem. Rev*. 2002; **102**: 835–854.
3. Samdal S, Volden HV, Ferro VR, García de la Vega JM, González-Rodríguez D and Torres T. *J. Phys. Chem. A* 2007; **111**: 4542–4550.
4. Claessens CG and Torres T. *Eur. J. Org. Chem.* 2000; **2000**: 1603–1607.
5. del Rey B, Keller U, Torres T, Rojo G, Agulló-López F, Nonell S, Marti C, Brasselet S, Ledoux I and Zyss J. *J. Am. Chem. Soc.* 1998; **120**: 12808–12817.
6. a) Díaz DD, Bolink HJ, Capelli L, Claessens CG, Coronado E and Torres T. *Tetrahedron Lett.* 2007; **48**: 4657–4660. b) Gommans H, Aeronouts T, Verreet B, Heremans P, Medina A, Claessens CG and Torres T. *Adv. Func. Mater.* 2009; **19**: 3435–3439. c) Rubio N, Jiménez-Banzo A, Torres T and Nonell S. *J. Photochem. Photobiol. A* 2007; **185**: 214–219.
7. González-Rodríguez D, Carbonell E, De Miguel Rojas G, Atienza Castellanos C, Guldi DM and Torres T. *J. Am. Chem. Soc.* 2010; **132**: 16488–16500.
8. a) del Rey B and Torres T. *Tetrahedron Lett.* 1997; **38**: 5351–5354. b) Claessens CG and Torres T. *J. Am. Chem. Soc.* 2002; **124**: 14522–14523. c) Gonzalez-Rodriguez D, Torres T, Olmstead MM, Rivera J, Herranz MA, Echegoyen L, Castellanos CA and Guldi DM. *J. Am. Chem. Soc.* 2006; **128**: 10680–10681.
9. Kobayashi N, Kondo R, Nakajima S and Osa T. *J. Am. Chem. Soc.* 1990; **112**: 9640–9641.
10. a) El- Khouly ME, Shim SH, Araki Y, Ito O and Ksy K-Y. *J. Phys. Chem.* 2008; **12**: 3910–3917. b) Kim JH, El-Khouly ME, Araki Y, Ito O and Kay KY. *Chem. Lett.* 2008; **37**: 544–545.
11. a) Yu Tolbin A and Tomilova LG. *Russ. Chem. Rev*. 2011; **80**: 531–551. b) Guilleme J, González-Rodríguez D and Torrs T. *Angew. Chem. Int. Ed*. 2011; **50**: 33506–33509. c) Morse GE and Bender TP. *Inorg. Chem*. 2012; **51**: 6460–6467.
12. Gonzalez-Rodríguez D, Torres T, Guldi DM, Rivera J and Echegoyen L. *Org. Lett.* 2002; **4**: 335–338.
13. a) Eckert AK, Salomé Rodríguez-Morgade MS and Torres T. *Chem. Commun.* 2007; 4104–4106. b) Jacquot de Rouville HP, Garbage R, Ample F, Nickel A, Meyer J, Moresco F, Joachim C and Rapenne G. *Chem. Eur. J.* 2012; **18**: 8925–8928.
14. Claessens CG, Gonzalez-Rodriguez D, del Rey B, Torres T, Mark G, Schuchmann H-P, von Sonntag C, MacDonald JG and Nohr RS. *Eur J. Org. Chem*. 2003; **2003**: 2547–2551.
15. a) Martin G, Rojo G, Agulló-López F, Torres T, Ferro VR and Garcia de la Vega JM. *J. Phys. Chem. B*. 2002; **106**: 13139–13145. b) Dabak S, Gul A and Bekaroglu O. *Chem. Ber.* 1994; **127**: 2009–2012.
16. Gonzalez-Rodriguez D and Torres T. *J. Organomet. Chem.* 2009; **694**: 1617–1622.
17. Potz R, Goldner M, Huckstadt H, Cornelissen U, Tutab A and Homborg H. *Anorg. Allg. Chem.* 2000; **626**: 588–596.
18. Gonzalez-Rodriguez D, Victoria Martinez-Diaz MV, Abel J, Perl A, Huskens J, Echegoyen L and Torres T. *Org. Lett.* 2010; **12**: 2970–2973.