Pergamon

Tetrahedron Letters, Vol. 38, No. 30, pp. 5351-5354, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)01170-2

Synthesis of Highly Conjugated Boron (III) Subphthalocyanines

Belén del Rey and Tomás Torres*

Dpto. de Química Orgánica (C-I), Facultad de Ciencias, Universidad Autónoma de Madrid,
28049, Madrid, Spain.

Abstract: Metal-mediated cross-coupling of alkynes has been applied for the first time to C-C bond formation in Subphthalocyanines. Triiodosubphthalocyanine **1** was reacted with the corresponding terminal alkyne in the presence of bis[triphenylphosphine]palladium (II) dichloride and copper (I) iodide to give the corresponding highly conjugated alkynyl subphthalocyanines **2-5** in 25-30% yield.
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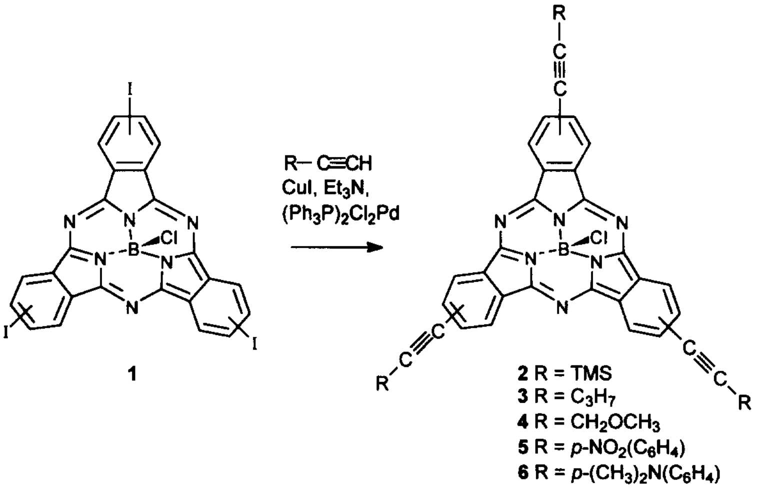
Subphthalocyanines (SubPcs),[1] such as **1-6**, are macrocyclic complexes composed of three isoindoline units containing boron as the central atom which have been used as intermediates for the synthesis of unsymmetrically substituted phthalocyanines (Pcs).[2-4]

This kind of Pc-related compounds displays a Hückel aromatic delocalized 14 π-electron system and has a cone-shaped singular geometry,[5] which makes these molecules also attractive as targets for nonlinear optical (NLO) applications.[6] Thus, some SubPcs present very large second-order molecular polarizabilities (β) mostly associated with the octupolar contribution.[7,8]



1

2 R = TMS
3 R = C_3H_7
4 R = CH_2OCH_3
5 R = p-$NO_2(C_6H_4)$
6 R = p-$(CH_3)_2N(C_6H_4)$

SubPcs are prepared by cyclotrimerization reaction of a phthalonitrile in the presence of a borane such as BX_3, BAr_3 or BR_3.[1] The high reactivity of the boron derivatives with many functional groups precludes the use of this method for introducing different peripheral substituents on the SubPc ring. For this reason only SubPcs having certain types of substituents such as *tert*-butyl, nitro, iodo, tioether, sulfone and sulphonic acid have been prepared until now.[1,3b]

For all the above mentioned reasons the development of efficient new methods for the synthesis of functionalized SubPcs is becoming an important goal. In the present letter the well-known metal-mediated cross-coupling of alkynes is applied for the first time to the preparation of alkynyl substituted SubPcs **2-5**. Moreover this strategy is used here for synthesizing compound **5**, the first representative of a new class of highly conjugated SubPcs featuring push-pull arylethynyl structural motifs especially designed for studying their second-order nonlinear optical (NLO) properties.[9] No examples of C-C bond formation in SubPcs have been hitherto described.[10]

Typically, triiodosubphthalocyanine **1**[1] (1 mmol) was reacted with the corresponding terminal alkyne (3.6 mmol) in the presence of bis[triphenylphosphine]palladium (II) dichloride (0.03 mmol) and copper (I) iodide (0.0015 mmol) in triethylamine (10 ml)[11] at room temperature under argon to yield the corresponding alkynyl subphthalocyanine **2-5**[12] after chromatographic separation. The reaction was monitored by TLC. Reaction times vary from 1.5 h, in the case of compound **5**, to 42 h, for compound **4**.[12]

The absence of oxygen in these reactions is essential in order to prevent the formation of homocoupling compounds from the terminal alkyne. An aprotic amine should be used as solvent in this kind of reaction, because the employment of piperidine or diethylamine, for example, led to ring opening and decomposition of subphthalocyanine **1**.

Compound **6** could not be obtained by this method. The low reactivity of compound **1** with *p*-dimethylaminoethynylbenzene facilitates the homocoupling side reaction of the alkyne to afford 1,4-dimethylaminophenylbutadiyne as main product with partial recovery of the starting material **1**.

Subphthalocyanines **2-5** were characterized by ^{1}H-NMR, IR, FAB-MS and UV-visible.[12] Analytical data were consistent with the proposed structures. Compounds **2-5** are actually mixtures of two isomers, with C_1 and C_3 symmetries, since the starting compound is also a regioisomeric mixture.[1] The ratio of isomers could not be determined by ^{1}H-NMR, but a 3:1 ratio favorable to the C_1 isomer is expected considering the statistical method used in the preparation of **1**.[1]

All compounds show in ^{1}H-NMR three typical groups of aromatic signals betwen 9.1 and 8.0 ppm corresponding to the distinct protons of the subphthalocyanine.

Figure 1 shows the UV-visible spectrum of ethynyl derivative **3** as a representative example in comparison with that of the starting material **1**. The Soret (B) transition occurring in the blue region of the spectrum, centered at 314 nm in **1**, is shifted to a higher wavelength, at 345 nm, in compound **3**, whereas a new intense band appears at 275 nm due to the presence of the triple bond. On the other hand, the absorption maximum of the Q-band, that is centered at 574 nm in **1**, is red-shifted in **3** (583 nm) as a consequence of the extended conjugation. Compound **5**, with higher conjugation, presents a Q-band at 590 nm.[12]

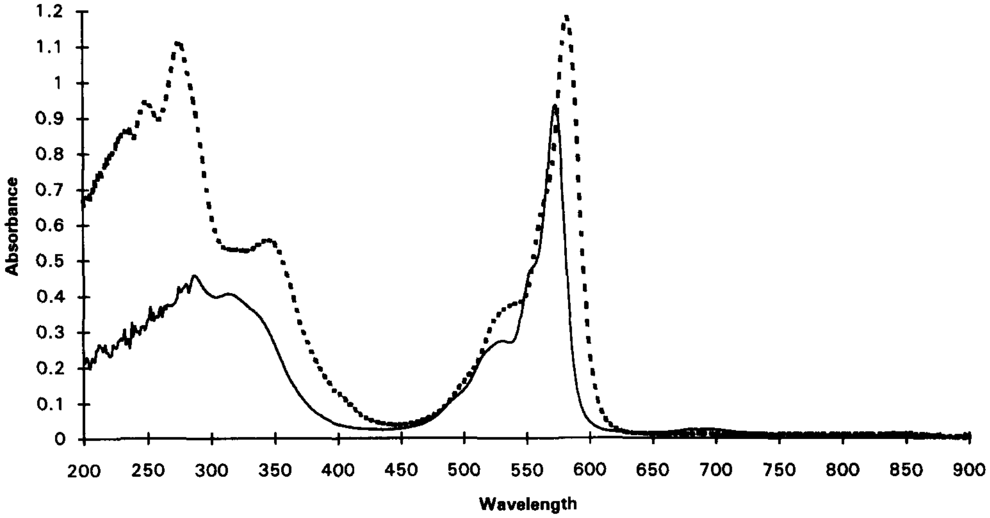


Fig 1: UV-visible spectra of subphthalocyanines **1** (—) and **3** (- - -) in chloroform solution ($2.8x10^{-5}$ M).

The results of our investigations indicate that metal-mediated cross-coupling of alkynes is compatible with the boron (III) subphthalocyanine system, thus providing a convenient method for the peripheral functionalization of this kind of compounds.[13] On the other hand, compound **5** has shown high first order hyperpolarizability values in solution measured by the HRS (Hyper-Rayleigh Scattering) technique. For this reason new highly conjugated SubPcs having arylethynyl subunits are being presently prepared for studying their NLO properties.

Acknowledgements

This work was supported by CICYT (Spain) and the Comunidad Autónoma de Madrid through grants MAT96/0654, TIC 96-0668 and 06T/017/96 respectively, and by the EC through Grant ERBCHRX-CT94-0558.

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10. Carbon-carbon bond formation in related compounds following metal-mediated cross-coupling of alkynes has been largely reported in the case of porphyrins (see for example Nishino, N.; Wagner, R. W.; Lindsey, J. S.; *J. Org. Chem* **1996,** *61*, 7534 and Lecours, S. M.; Guan, H-V.; DiMagno, S. G.; Wang, C. H.; Therein, M. J.; *J. Am. Chem. Soc.* **1996,** *118*, 1497) and only recently reported in phthalocyanines (Ali, H.; Van Lier, J. E.; *Tetrahedron Lett.* **1997,** *38*, 1157 and Maya, E.; Vázquez, P.; Torres, T.; *Chem. Commun.* in press).
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12. Selected data for alkynylsubphthalocyanines:

    2: Reaction time: 5 h; aluminium oxide (10% H_2O); ethyl acetate-n-hexane (1:2); Yield: 28%, m.p.> 200°C. ^{1}H- NMR (200 MHz, $CDCl_3$) δ 9.0 (m, 1H, Ar), 8.8 (m, 1H, Ar), 8.0 (m, 1H, Ar), 0.35 (s, 9H, CH_3) ppm; FAB-MS (3-NOBA) *m/z* 718 [M^+], 683 [$(M-Cl)^+$]; IR (KBr) ν 3426 (NC), 2200 (C≡C), 1726 (CN), 1455 (B-N), 1098 (B-Cl) cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε/dm^3 mol^{-1} cm^{-1}) 583 (4.6), 530 (sh), 345 (4.3), 276 (4.6) nm.

    3: Reaction time: 20 h; silica gel; CH_2Cl_2; Yield: 28%, m.p.> 200°C. ^{1}H- NMR (200 MHz, $CDCl_3$) δ 8.9 (s, 1H, Ar), 8.7 (m, 1H, Ar), 7.9 (m, 1H, Ar), 2.5 (t, 2H, CH_2), 1.7 (q, 2H, CH_2), 2.5 (t, 3H, CH_3) ppm; FAB-MS (3-NOBA) *m/z* 628 [M^+], 593 [$(M-Cl)^+$]; IR (KBr) ν 3436 (NC), 2333 (C≡C), 1613 (CN), 1443 (B-N), 830 (B-Cl), 786 (Si-C) cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε/dm^3 mol^{-1} cm^{-1}) 583 (4.5), 530 (sh), 345 (4.2), 275 (4.5) nm.

    4: Reaction time: 42 h; aluminium oxide (10% H_2O); CH_2Cl_2; Yield: 26%, m.p.> 200°C. ^{1}H- NMR (200 MHz, $CDCl_3$) δ 8.97 (s, 1H, Ar), 8.8 (m, 1H, Ar), 8.0 (m, 1H, Ar), 4.4 (s, 2H, CH_2), 3.6 (s, 3H, CH_3) ppm; FAB-MS (3-NOBA) *m/z* 634 [M^+], 599 [$(M-Cl)^+$]; IR (KBr) ν 3100 (NC), 2155 (C≡C), 1613 (CN), 1450 (B-N), 1127 and 1095 (C-O-C), 867 (B-Cl) cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε/dm^3 mol^{-1} cm^{-1}) 577 (4.3), 530 (sh), 325 (4.2), 269 (4.5) nm.

    5: Reaction time: 1.5 h; silica gel; CH_2Cl_2; Yield: 29%, m.p.> 200°C. ^{1}H- NMR (200 MHz, $CDCl_3$) δ 9.1 (m, 1H, Ar), 8.9 (m, 1H, Ar), 8.1 (m, 1H, Ar), 8.3 and 7. 8 (AA'BB' system, 4H) ppm; FAB-MS (3-NOBA) *m/z* 865 [M^+], 830 [$(M-Cl)^+$]; IR (KBr) ν 2210 (C≡C), 1592 (CN), 1331 (NO_2), 1185 (B-N), 854 (B-Cl) cm^{-1}; UV/vis ($CHCl_3$) λ_{max} (log ε/dm^3 mol^{-1} cm^{-1}) 590 (4.6), 540 (sh), 355 (4.5), 285 (4.6) nm.
13. For example, Subpcs bearing ether groups, such as **4**, had not been described until now.

(*Received in UK* 12 *May* 1997; *revised* 12 *June* 1997; *accepted* 13 *June* 1997)