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Article

Synthesis, Characterization, and UV–vis Linear Absorption of Centrosymmetric π-Systems Incorporating *closo*-Dodecaborate Clusters

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Single- and multibranched centrosymmetric derivatives incorporating B_{12} clusters $[B_{12}H_{11}-N(H)=C(H)-C_6H_4-C_6H_4-C(H)=(H)N-B_{12}H_{11}]^{2-}$ (**3**) and $[1,3,5-(4-(B_{12}H_{11}-N(H)=C(H))-C_6H_4)-C_6H_3]^{3-}$ (**5**) have been synthesized. Both derivatives were characterized by multinuclear NMR and ESI-MS analyses. To the best of our knowledge, compound **5** is the first example of a multicage derivative bearing three B_{12} units. Compounds **3** and **5** are only slightly yellowish colored. The UV–vis absorption curves of **3** and **5** show intense absorption bands at 360 and 314 nm, respectively. This result permits us to confirm the strong donor effect of the B_{12} cluster. The hypsochrome effect observed for compound **5** compared to that of compound **3** confirms the interest in multibranched derivatives for the preparation of two-photon absorption materials active in the visible range.

Introduction

The dodecahydro-*closo*-dodecaborate dianion $[B_{12}H_{12}]^{2-}$ occupies an important place in the field of inorganic cluster chemistry with respect to its unique structure of a regular icosahedron, its high thermal stability, low toxicity, and remarkable chemical and hydrolytical stability. Several routes to substituted *closo*-B_{12} anions have been studied, including the formation of *exo*-boron−nitrogen,[1,2] −oxygen,[3−5] −sulfur,[6] −halogen,[7] −phosphorus,[8] and −carbon bonds.[9,10] The chemistry of $[B_{12}H_{12}]^{2-}$, together with its potential and/or demonstrated applications, were reviewed in 2002.[11] The main applications of *closo*-B_{12} derivatives are related to the biomedical and environmental fields. For instance, some functionalized B_{12} clusters are valuable candidates for boron neutron capture therapy (BNCT), a method for the treatment of cancer based on the interaction of ^{10}B and thermal neutrons.[12] Another example is with the selective extraction of various trivalent radionuclides from nuclear waste arising from the PUREX process.[13]

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Besides these applications and on the basis of the unique electronic structure of these derivatives, the optical properties of boron-containing 12-vertex clusters have recently received much attention. In 1999, the potentialities of *closo*-$[B_{12}H_{12}]^{2-}$ as building blocks for liquid crystal materials were investigated by Kaszynski et al.[14] More recently, Jelliss et al. observed unexpected luminescence from a luthenacarborane complex.[15] Marder et al. reviewed boron-containing second-order nonlinear optical (NLO) materials.[16,17] These authors underlined that efforts are mainly devoted to the incorporation of three-coordinate boron atoms as acceptors into π-systems.[16,18,19] In contrast, relatively little works have focused on the incorporation of 12-vertex clusters into π-systems. Within this field, precursor works have been performed with the calculation and/or measurement of large first hyperpolarizability (β) values for derivatives of 1-carba-*closo*-dodecaborate anion, $[CB_{11}H_{12}]^-$, and *o*-, *m*-, or *p*-carborane, $C_2B_{10}H_{12}$.[20−24] Besides second-order NLO materials, the two-photon absorption (2PA or TPA) process is a three-order NLO process in which materials simultaneously absorb two photons. Materials exhibiting both a large two-photon cross section and up-conversion properties can find applications in various fields, for instance, as optical limiters,[25,26] three-dimensional optical data storage,[27] and microfabrication.[28] Within this field, the synthesis of non-centrosymmetric π-systems incorporating *closo*-B_{12} clusters

was performed by our group in 2005.[29] The donor effect of the *closo*-B_{12} cluster was clearly demonstrated by UV−vis linear absorption studies of various π-systems. To the best of our knowledge, the non-centrosymmetric anion [NC−C_6H_4−C(H)=C(H)−C_6H_4−C(H)=N(H)−$B_{12}H_{11}]^-$, exhibiting a stilbene unit as π-transmitter and a CN group as acceptor, was the first B_{12}-containing derivative showing TPA properties. On the basis of these previous works, we focused our attention in the present paper on the synthesis and characterization of centrosymmetric π-systems incorporating *closo*-B_{12} units. The development of such compounds seems interesting for two reasons. First, there are, to the best of our knowledge, only two papers reporting the synthesis of derivatives incorporating more than one B_{12} units. Wellum et al. have prepared $[B_{12}H_{11}$−S−S−$B_{12}H_{11}]$-Cs_4 by oxidation of $[B_{12}H_{11}SH]^{2-}$.[30] By treatment of $[B_{12}H_{11}(OH)]^{2-}$ with organic and inorganic acid dichlorides in acetonitrile, Preetz et al. have synthesized the bridged compounds $[B_{12}H_{11}(ox)B_{12}H_{11})]^{,4-}$ $[B_{12}H_{11}(p\text{-}OOCC_6H_4\text{-}COO)B_{12}H_{11}]^{,4-}$ $[B_{12}H_{11}(m\text{-}OOCC_6H_4COO)B_{12}H_{11}]^{,4-}$ $[B_{12}H_{11}(SO_3)\text{-}B_{12}H_{11}]^{,4-}$ and $[B_{12}H_{11}(SO_4)B_{12}H_{11}]^{.4-31}$ Therefore, the synthesis of derivatives containing more than two B_{12} units has never been reported. Moreover, the bonding of the B_{12} cage by π-spacer has never been described. Second, centrosymmetric derivatives are more appropriate than non-centrosymmetric ones for TPA applications in the visible range, because of lower coloration.[32,33] Moreover, recent studies have shown interest in multibranched systems that are characterized by hypsochrome and hyperchrome effects compared to corresponding quadrupolar systems.[34] It was also reported that the presence of donor groups at the extremity of each arm increased the TPA properties.[35]

Experimental Section

General Considerations. Moisture sensitive reactions were carried out under an atmosphere of pure argon using vacuum-line and Schlenk techniques with solvents purified by standard methods.[36] $(Et_3NH)_2[B_{12}H_{12}]$ was purchased from KATCHEM Ltd., Prague, and used without further purification. ^1H, ^{13}C, and ^{11}B NMR spectra were recorded on a Bruker AM 300 spectrometer at 300, 75, and 96.29 MHz, respectively, with $Et_2O \cdot BF_3$ as the external reference (positive values downfield). Some NMR spectra are

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available in the Supporting Information. The infrared spectra were recorded on a FTIR Nicollet Magna 550 spectrometer. High-resolution mass spectra of ionic species were measured on an Esquire 3000 ion trap system and, alternatively, on a Bruker Esquire-LC ion trap instrument using electrospray ionization. Negative ions were detected. Samples dissolved in acetonitrile (1 ng μL^{-1}) were introduced to the ion source by infusion of 3 μL min^{-1}; the drying temperature was 300 °C, drying gas flow 5 L min^{-1}, and nebulizing gas pressure 10 psi. UV−vis linear absorption curves were recorded in acetonitrile solution (10 mm cell) on a Varian CARY 1E spectrometer. Differential scanning calorimetry (DSC) analyses were performed on a TA8000 Mettler-Toledo apparatus.

Synthesis of [$B_{12}H_{11}$−N(H)=C(H)−C_6H_4−C(H)O][N(n-Bu)$_4$], [2][N(n-Bu)$_4$]. The monoamino derivative [$B_{12}H_{11}NH_3$]$^-$ (**1**) was prepared from [$B_{12}H_{12}$]$^{2-}$ as described by Hertler and Raasch.[37] In a typical experiment, 0.033 g (0.25 mmol) of terephthalaldehyde and 0.399 g (1 mmol) of [**1**][N(n-Bu)$_4$] were dissolved in 10 mL of dichloromethane. A few drops of an aqueous solution of sodium hydroxide (5 wt %) were added to the mixture. The reaction mixture was stirred at room temperature for 8 h. Finally, the solvent was removed in a vacuum and the crude product was purified by chromatography on silica gel using pure CH_2Cl_2 and then a 6:1 CH_2Cl_2:CH_3CN mixture. The first colorless fraction was identified as unreacted terephthalaldehyde. The second yellowish fraction yielded 0.026 g (0.05 mmol, 20%) of pure compound [**2**][N(n-Bu)$_4$]. The third fraction corresponded to unreacted [$B_{12}H_{11}NH_3$]$^-$.

^1H NMR (ppm, CD$_3$CN): δ 0.2−2 (unresolved, B-H), 1.04 (t, 12H, N−(CH$_2$)$_3$CH_3), 1.48 (m, 8H, N−(CH$_2$)$_2$−CH_2−CH$_3$), 1.66 (m, 8H, N−CH$_2$−CH_2−CH$_2$−CH$_3$), 3.04 (t, 8H, N−CH_2−(CH$_2$)$_2$−CH$_3$), 7.92 (d, 2H, C$_6H_4$), 8.04 (d, 2H, C$_6H_4$), 8.87 (d, 1H, HN=CH, $^3J_{H-H}$ = 19.0 Hz), 10.15 (s, 1H, CHO), 10.76 (d, 1H, HN=CH). ^{11}B−NMR (ppm, CH$_3$CN): δ −3.73 (s, 1B), −14.78 (d, 11B, J_{B-H} = 128.5 Hz). ^{13}C NMR (ppm, CD$_2$Cl$_2$): δ 13.14 (4C, N−(CH$_2$)$_3$CH_3), 20.09 (4C, N−(CH$_2$)$_2$−CH$_2$−CH$_3$), 24.32 (4C, N−CH$_2$−CH$_2$−CH$_2$−CH$_3$), 59.36 (4C, N−CH$_2$−(CH$_2$)$_2$−CH$_3$), 130.45 (4C, C_6H_4), 133.32 (1Cq, C_6H_4), 141.07 (1Cq, C_6H_4), 169.13 (1C, HC=NH), 192.06 (1C, CHO). m/z (ESI-MS) 273 (M$^-$). DSC anal.: strong exothermic effect starting at 238 °C.

Synthesis of [$B_{12}H_{11}$−N(H)=C(H)−C_6H_4−C_6H_4−C(H)=(H)-N−$B_{12}H_{11}$][N(n-Bu)$_4$]$_2$, [3][N(n-Bu)$_4$]$_2$. In a first step, 0.077 g (0.51 mmol) of p-formylphenylboronic acid and 0.005 g (3.9 10^{-5} mol) of palladium(II) acetate were dissolved in 8 mL of an aqueous ethanol solution (95%). Next, 0.3 mL (0.6 mmol) of an aqueous solution of sodium carbonate (2 M) was added to the ensuing solution. The reaction mixture was stirred for 8 h at room temperature. The solvent was subsequently removed under a vacuum. The resulting crude product was purified by chromatography on silica gel using a 4:1 CH_2Cl_2:CH_3CN solution, yielding 0.032 g (0.153 mmol, 64%) of p-p'-diformylbiphenyl (**4**).

Anal. Found: C, 79.0; O, 15.7; H, 5.1. Calcd for **4**: C, 79.9; O, 15.2; H, 4.8. ^1H NMR (ppm, CD$_2$Cl$_2$): δ 7.94 (d, 4H, C$_6H_4$, $^3J_{H-H}$ =8.67 Hz), 8.03 (d, 4H, C$_6H_4$, $^3J_{H-H}$ =8.67 Hz), 9.99 (s, 2H, CHO). ^{13}C NMR (ppm, CD$_3$CN): δ 127.61 (4C, C_6H_4), 129.61 (4C, C_6H_4), 136.63 (2Cq, C_6H_4), 145.54 (2Cq, C_6H_4), 191.78 (2C, CHO). FTIR (v_{max}, cm^{-1}): 1683 (C=O), 1601 (C=C). DSC anal.: mp 146 °C, strong exothermic effect starting at 160 °C.

In a second step, 0.798 g (0.002 mol) of [**1**][N(n-Bu)$_4$] was added to a solution of 0.210 g (0.001 mol) of **4** in 8 mL of dimethylfor-mamide. A few drops of an aqueous solution of sodium hydroxide (5 wt %) were added. The reaction mixture was stirred at room

temperature for 16 h. The solvent was removed in a vacuum, and crude product was purified by chromatography on silica gel using a 4:1 CH_2Cl_2:CH_3CN solution, yielding 0.398 g (0.4 mmol, 40%) of [$B_{12}H_{11}$−N(H)=C(H)−C_6H_4−C_6H_4−C(H)=(H)N−$B_{12}H_{11}$][N-(n-Bu)$_4$]$_2$, [**3**][N(n-Bu)$_4$]$_2$.

^1H NMR (ppm, CD$_2$Cl$_2$): δ 0.2−2 (unresolved, B-H), 0.98 (t, 24H, N−(CH$_2$)$_3$CH_3), 1.38 (m, 16H, N−(CH$_2$)$_2$−CH_2−CH$_3$), 1.61 (m, 16H, N−CH$_2$−CH_2−CH$_2$−CH$_3$), 3.06 (t, 16H, N−CH_2−(CH$_2$)$_2$−CH$_3$), 7.95 (s, 8H, C$_6H_4$), 8.82 (d, 2H, HN=CH, $^3J_{H-H}$ =20.0 Hz), 9.86 (d, 2H, HN=CH). ^{13}C NMR (ppm, CD$_2$Cl$_2$): δ 13.14 (8C, N−(CH$_2$)$_3$CH_3), 20.09 (8C, N−(CH$_2$)$_2$−CH$_2$−CH$_3$), 24.32 (8C, N−CH$_2$−CH$_2$−CH$_2$−CH$_3$), 59.36 (8C, N−CH$_2$−(CH$_2$)$_2$−CH$_3$), 129.61 (4C, C_6H_4), 131.00 (4C, C_6H_4), 143.85 (4Cq, C_6H_4), 169.14 (2C, HN=CH). m/z (ESI-MS) 244.5 (M^{2-}/2). DSC anal.: strong exothermic effect starting at 260 °C.

Synthesis of [1,3,5-(4-($B_{12}H_{11}$−N(H)=C(H))−C_6H_4)−C_6H_3]-[N(n-Bu)$_4$]$_3$, [5][N(n-Bu)$_4$]$_3$. In a first step, 1,3,5-(4-bromophenyl)-benzene was synthesized using the method described by Palomero et al.[38] In a second step, 1,3,5-(4-formylphenyl)benzene was obtained from 1,3,5-(4-bromophenyl)benzene using the procedure described by Wekber et al.[39] In a third step, 1.195 g (0.5 mmol) of 1,3,5-(4-formylphenyl)benzene and 1.197 g (0.003 mol) of [**1**][N(n-Bu)$_4$] were dissolved in 20 mL of dimethylformamide. A few drops of an aqueous solution of sodium hydroxide (5 M) were added to the reaction mixture. The solution was subsequently stirred at room temperature for 72 h. The solvent was removed in a vacuum. A drop of 20 mL of a 1:4 water:methanol mixture was added to the solution, yielding crude [1,3,5-(4-($B_{12}H_{11}$−N(H)=C(H))−C_6H_4)−C_6H_3][N(n-Bu)$_4$]$_3$, [**5**][N(n-Bu)$_4$]$_3$, to precipitate. The ensu-ing solid was filtered and further purified by chromatography on silica gel using CH_2Cl_2 then 1:4 CH_3CN:CH_2Cl_2 yielded 0.429 g (0.28 mmol, 55%) of pure [**5**][N(n-Bu)$_4$]$_3$.

^1H NMR (ppm, (CD$_3$)$_2$SO): δ 0.2−2 (unresolved, B-H), 0.93 (t, 36H, N−(CH$_2$)$_3$CH_3), 1.31 (m, 24H, N−(CH$_2$)$_2$−CH_2−CH$_3$), 1.56 (m, 24H, N−CH$_2$−CH_2−CH$_2$−CH$_3$), 3.16 (t, 24H, N−CH_2−(CH$_2$)$_2$−CH$_3$), 8.25 (d, 6H, C$_6H_4$), 8.30 (s, 3H, C$_6H_3$), 8.41 (d, 6H, C$_6H_4$), 8.70 (s, 3H, HC=NH), 12.17 (s, 3H, HC=NH). ^{11}B−NMR (ppm, CH$_3$CN): δ −3.82 (s, 1B), −15.35 (d, 11B, J_{B-H} = 128.5 Hz). ^{13}C NMR (ppm, CD$_2$Cl$_2$): δ 13.14 (12C, N−(CH$_2$)$_3$CH_3), 20.09 (12C, N−(CH$_2$)$_2$−CH$_2$−CH$_3$), 24.32 (12C, N−CH$_2$−CH$_2$−CH$_2$−CH$_3$), 59.36 (12C, N−CH$_2$−(CH$_2$)$_2$−CH$_3$), 127.33 (3C, C_6H_3), 128.61 (3Cq, C_6H_3), 129,06 (6C, C_6H_4), 131,07 (6C, C_6H_4), 141.22 (3Cq, C_6H_4), 147.60 (3Cq, C_6H_4), 169.30 (3C, HC=NH). FTIR (v_{max}, cm^{-1}): 3243 and 3148 (N−H), 2487 (B−H), 1653 (C=N). m/z (ESI-MS) 270 (M^{3-}/3).

Results and Discussion

Synthesis and Characterization of Centrosymmetric π-Systems Incorporating B$_{12}$ Clusters. In a previous paper, we showed that the formation of Schiff bases is a convenient route to connect π-systems with B$_{12}$ clusters.[29] Indeed, Sivaev et al. have established that the monoamino derivative of the *closo*-dodecaborate cluster, [$B_{12}H_{11}NH_3$]$^-$, can react with various arylaldehydes, R−C_6H_4−CHO, to yield the corre-sponding iminium derivative [R−C_6H_4−C(H)=N(H)−$B_{12}H_{11}$]$^-$.[40] The synthesis of centrosymmetric π-systems was

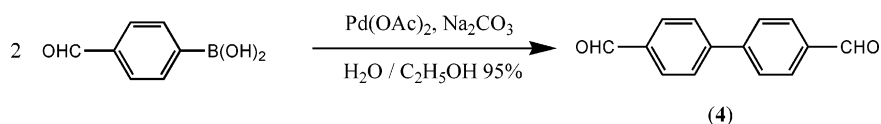(37) Hertler, R.; Raasch, M. S. *J. Am. Chem. Soc.* **1964**, *86*, 3661.

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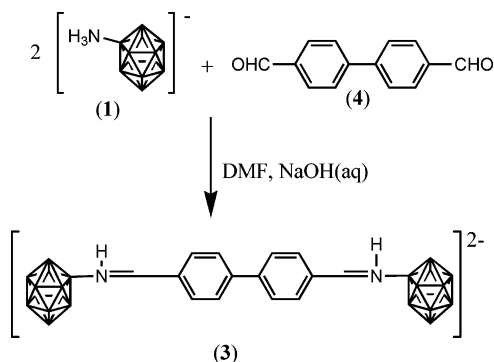(39) Weber, E.; Hecker, M.; Koepp, E.; Orlia, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1251.

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Scheme 1

$$2 \quad \text{OHC}-\text{C}_6\text{H}_4-\text{B(OH)}_2 \xrightarrow[\text{H}_2\text{O / C}_2\text{H}_5\text{OH 95\%}]{\text{Pd(OAc)}_2,\ \text{Na}_2\text{CO}_3} \text{OHC}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CHO}$$

(4)

Scheme 2

$$2 \begin{bmatrix} \text{H}_3\text{N}-\text{B}_{12} \end{bmatrix}^- + \text{OHC}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CHO}$$

(1)   **(4)**

DMF, NaOH(aq)

(3)

thus conducted using this same synthetic pathway. On this basis, we first envisaged the preparation of a simple centrosymmetric π-system incorporating B_{12} clusters, namely a phenyl ring p-substituted with two B_{12} units.

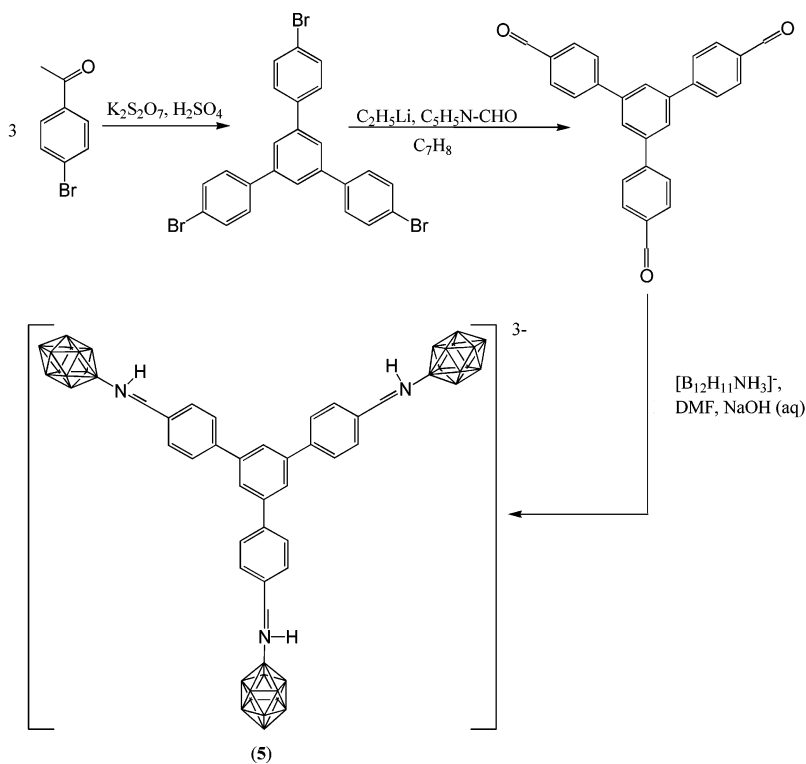As we found, the reaction of an excess of $[B_{12}H_{11}NH_3]^-$ (**1**) with terephthalaldehyde, $O(H)C-C_6H_4-C(H)O$, in the presence of a catalytic amount of sodium hydroxide did not give the expected dianion, $[B_{12}H_{11}-N(H)=C(H)\text{-}C_6H_4-C(H)=N(H)-B_{12}H_{11}]^{2-}$. Besides unreacted starting products, purification by chromatography on silica gel permitted us to isolate only the monoanion $[B_{12}H_{11}-N(H)=C(H)-C_6H_4-C(H)O]^-$ (**2**) with a low yield (20%). This derivative was characterized by ^1H, ^{13}C, and ^{11}B NMR analyses. The structure of **2** deduced from the NMR data was confirmed

by ESI-MS analysis with the observation of the molecular peak at $m/z = 273$. It appears therefore that the reactivity of the formyl group of **2** was drastically reduced compared to that of starting terephthalaldehyde. This can be attributed to a strong donor effect of the B_{12} cluster located in the para position. This low reactivity was not observed by Preetz et al. during the synthesis of $[B_{12}H_{11}-OC(O)-C_6H_4-C(O)O-B_{12}H_{11}]$,[4−31] which can be related to the presence of a carbonyl group between each B_{12} cluster and central ring. To soften this effect, we decide to enhance the size of the π-linker between the two formyl groups. For that purpose and on the basis of the works of Smith et al.,[41] we first prepare p,p'-diformylbiphenyl, $O(H)C-C_6H_4-C_6H_4-C(H)O$ (**4**), from $O(H)C-C_6H_4-B(OH)_2$ via a Suzuki cross-coupling reaction (Scheme 1).
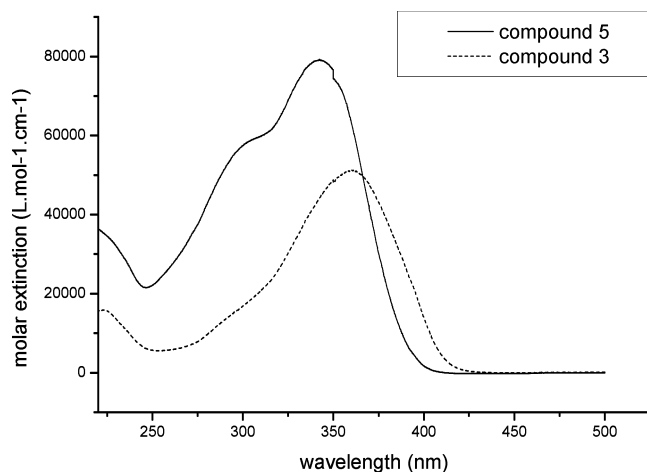
In a second step, the reaction of a molar excess of monoamino derivative **1** with **4** in the presence of a catalytic amount of sodium hydroxide gave $[B_{12}H_{11}-N(H)=C(H)-C_6H_4-C_6H_4-C(H)=(H)N-B_{12}H_{11}][N(n\text{-Bu})_4]_2$, $[\mathbf{3}][N(n\text{-Bu})_4]_2$, in 40% yield (Scheme 2).

Compound **3** was characterized by multinuclear NMR and ESI-MS analyses. In its ^1H NMR spectrum, the singlet at 9.99 ppm corresponding to the two formyl groups of **4** was replaced by two doublets at 8.82 and 9.86 ppm that corresponded to the protons of the two iminium $HC=NH$ bonds. Moreover, the relative intensity of the signals corresponding to the tetrabutylammonium and the phenyl ring

Scheme 3

$$3\ \text{CH}_3\text{CO}-\text{C}_6\text{H}_4-\text{Br} \xrightarrow{\text{K}_2\text{S}_2\text{O}_7,\ \text{H}_2\text{SO}_4} \xrightarrow[\text{C}_7\text{H}_8]{\text{C}_2\text{H}_5\text{Li},\ \text{C}_5\text{H}_5\text{N-CHO}}$$

$[B_{12}H_{11}NH_3]^-$, DMF, NaOH (aq)

(5)

Figure 1. Linear absorption spectra for compounds **3** and **5** (acetonitrile solution).

confirms the dianionic nature of **3**. The ^{13}C NMR spectrum of **3** is featured by a signal at 169.14 ppm that also corresponds to the two iminium HC=NH bonds, in replacement of the signal at 191.78 ppm that corresponded to the two formyl groups of **4**. It is interesting to note that all the quaternary-carbon atoms have the same chemical shift of 143.85 ppm, probably because of the high symmetry of the molecule. The structure of **3** deduced from the NMR data was unambiguously confirmed by ESI-MS analysis with the observation of a molecular peak at $m/z = 244.5$. Compound **3** as tetrabutylammonium salt is slightly yellowish and highly soluble in (dry) common organic solvents ($CHCl_3$, CH_2Cl_2, THF, acetone, CH_3CN, etc.). To the best of our knowledge, compound **3** is the first example of a π-system incorporating two B_{12} clusters.

In previous works, we observed that non-centrosymmetric π-systems incorporating B_{12} clusters, for instance, [NC−C_6H_4−C(H)=C(H)-C_6H_4−C(H)=N(H)−$B_{12}H_{11}$]$^-$, exhibit exceptional stabilities toward water and can be kept for a period of months.[29] It is important to notice that compound **3** is stable for months when kept under a dry atmosphere, but water vigorously decomposes [$B_{12}H_{11}$−N(H)=C(H)−C_6H_4−C_6H_4−C(H)=(H)N−$B_{12}H_{11}$]$^{2-}$, recovering starting compounds **1** and **4**. This lack of chemical stability drastically reduces its interest in terms of integration into materials for optical applications. This difference in behavior between the centrosymmetric and non-centrosymmetric derivatives may be attributed to a strong electron transfer between the acceptor and donor groups in the latter, which enhances the chemical stability of the corresponding imino bond.

Besides single-branched π-systems, multibranched π-systems have been demonstrated to show improved TPA properties, via a so-called cooperative enhancement effect.[34a] To study if some similar effect can be observed with B_{12}-containing compounds, we have investigated the synthesis of multibranched π-systems bearing three B_{12} clusters. On this basis, our idea was to synthesize a multibranched π-system analogue to compound **3**. For this purpose, we

Scheme 4. Schematic Drawing of 4,4′-(4-Methoxyphenyl(phenyl)amino)biphenyl
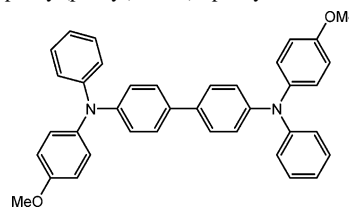
synthesized 1,3,5-(4-bromophenyl)benzene using the method described by J. Palomero et al.[38] In a second step, this derivative was converted to 1,3,5-(4-formylphenyl)benzene according to a known procedure.[39] As we found, the reaction of the latter with a molar excess of **1** gave [1,3,5-(4-($B_{12}H_{11}$−N(H)=C(H))−C_6H_4)−C_6H_3]$^{3-}$ (**5**) in a 55% yield after a purification step by chromatography (Scheme 3).

Similar to the results for other B_{12} derivatives, the attempts to grow single crystals from **5** remained unsuccessful. Octupolar compound **5** was characterized by multinuclear NMR and ESI-MS analyses. Beside the signals in the 0.2−3.2 ppm range featuring the B-H and methyl or methylene groups of the tetrabutylammonium ions, we observed one singlet at 8.3 ppm that was attributed to the benzene core of the π-system, C_6H_3, in good agreement with the values depicted for its organic analogues 1,3,5-(4-bromophenyl)-benzene and 1,3,5-(4-formylphenyl)benzene. The two doublets centered at 8.25 and 8.41 ppm were attributed to the aromatic protons of the three C_6H_4 groups. The two singlets at 8.70 and 12.17 ppm featured the iminium (H)C=N(H) bonds. The relative intensity of the different signals confirmed the trianionic nature of compound **5**. The structure of **5** deduced from the NMR data was confirmed by the observation of a molecular peak ($m/z = 270$) during the ESI-MS analysis. To the best of our knowledge, compound **5** is the first example of multicage compounds exhibiting three B_{12} units.

Consistent with compound **3**, compound **5** is only slightly colored (yellowish) and highly soluble in classical organic solvent but is decomposed by water, giving back the starting reactants 1,3,5-(4-formylphenyl)benzene and **1**.

UV−Vis Linear Absorption of the Centrosymmetric π-Systems Incorporating B_{12} Clusters. Figure 1 shows the UV−vis absorption curves in the molar extinction of compounds **3** and **5** in the 200−500 nm range.

Compound **3** exhibits an intense absorption band centered at 360 nm ($\epsilon_{max} = 51\,430$ L mol^{-1} cm^{-1}). The more intense coloration of **3** is due to the shift of the cutoff value to 425 nm. The pattern observed for the spectrum of **3** is in good agreement with those reported for biphenyl derivatives. Indeed, biphenyl ($C_{12}H_{10}$) shows an intense absorption band at 245 nm ($\epsilon_{max} = 12\,000$ L mol^{-1} cm^{-1}) attributed to π−π* transition.[42] In the case of biphenyl derivatives substituted with donor or acceptor groups, a red shift of the absorption band is usually observed. For instance, 4,4′-dimethoxybiphenyl shows an intense absorption band cen-

(41) Smith, K. A.; Campi, E. M.; Jackson, W. R.; Marcuccio, S.; Naeslund, G. M.; Deacon, G. B. *Synlett* **1997**, *1*, 131.

(42) Rao, C. N. R. *Ultra Violet and Visible Spectroscopy Chemical Application*; The Whitefriars Press: London, 1975.

tered at 263 nm ($\epsilon_{max} = 21\,700$ L mol^{-1} cm^{-1}), which corresponds to a red shift, $\Delta\lambda$, of 18 nm.[43] In the case of compound **3**, a red shift of $\Delta\lambda = 115$ nm is observed compared to biphenyl. This value should be related to the high donor effect of the B$_{12}$ units, in good agreement with previous results.[29] The value of the red shift obtained with **3** can be related to those obtained with bis-(diarylamino)-biphenyls.[32] Indeed, a shift of $+107$ nm has been measured for the 4,4′-(4-methoxyphenyl(phenyl)amino)biphenyl (Scheme 4).

The spectrum corresponding to compound **5** shows on Figure 1 an intense absorption band centered at 314 nm ($\epsilon_{max} = 78\,642$ L mol^{-1} cm^{-1}). We therefore observed a blue shift of the absorption band compared to compound **3** despite its having a more developed multibranched π-linker. Similar results have been observed by comparing quadrupolar and octupolar organic π-systems.[34d] The origin of this blue-shift phenomenon still remains unclear but clearly underlined this interest in quadrupolar derivatives, and by far dendrimers, for designing TPA materials transparent in the visible range. Despite these promising results deduced from the linear absorption behavior of these centrosymmetric derivatives incorporating B$_{12}$ clusters, their low stability toward hydrolysis precludes any interest in further optical analyses.

Conclusions

Single and multibranched centrosymmetric derivatives incorporating B$_{12}$ clusters [B$_{12}$H$_{11}$−N(H)=C(H)−C$_6$H$_4$−C$_6$H$_4$−C(H)=HN−B$_{12}$H$_{11}$]$^{2-}$ (**3**) and [1,3,5-(4-(B$_{12}$H$_{11}$−N(H)=C(H))−C$_6$H$_4$)−C$_6$H$_3$]$^{3-}$ (**5**) have been synthesized. To the best of our knowledge, compound **5** is the first example of multicage derivatives bearing three B$_{12}$ units. The UV−vis absorption curves of **3** and **5** permit us to confirm the strong donor effect of the B$_{12}$ cluster. The blue-shifted absorption band of **5** compared to **3** underlines the interest in multibranched derivatives for the preparation of TPA materials transparent in the visible range. The main drawback of these B$_{12}$-based derivatives is their low stability toward hydrolysis; further attention will now be focused on the preparation of centrosymmetric π-systems expected to show improved chemical stability.

Supporting Information Available: Some NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060563X

(43) Williamson, B.; Rodebush, W. H. *J. Am. Chem. Soc.* **1941**, *63*, 3018.