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Synthesis, characterization and optical properties of π -conjugated systems incorporating *closo*-dodecaborate clusters: new potential candidates for two-photon absorption processes[†]

R. Bernard,^{*a*} D. Cornu,^{**a*} P. L. Baldeck,^{*b*} J. Čáslavský,^{*c*} J.-M. Létoffé,^{*a*} J.-P. Scharff^{*a*} and P. Miele^{*a*}

- ^a Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615-Université Claude Bernard-Lyon 1, 43 Bd du 11 Novembre 1918, F-69622, Villeurbanne cedex, France. E-mail: David.Cornu@univ-lyon1.fr
- ^b Laboratoire de Spectrométrie Physique, UMR CNRS 5588-Université Joseph Fourier, 140 Avenue de la Physique-BP 87, F-38402, Saint Martin d'Hères, France
- ^c Institute of Analytical Chemistry, Czech Academy of Sciences, Veveří 97, 611 42, Brno, Czech Republic

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Non-centrosymmetric π -conjugated systems incorporating *closo*-dodecaborate clusters,

[NC-C₆H₄-C(H)=N(H)-B₁₂H₁₁]⁻ (2), [NC-C₆H₄-C(H)=C(H)-C₆H₄-C(H)=N(H)-B₁₂H₁₁]⁻ (3), and [NC-C₆H₄-C(H)=C(H)-C₆H₄-C(H)=C(H)-C₆H₄-C(H)=N(H)-B₁₂H₁₁]⁻ (4) have been synthesized by reaction of the monoamino derivative of B₁₂, [B₁₂H₁₁NH₃]⁻ (1), with various arylaldehydes, R-C₆H₄-CHO. These Schiff base-like compounds were fully characterized by multinuclear NMR spectroscopy and mass spectrometry. In order to evaluate these boron rich π -systems as potential materials for two-photon absorption (TPA) processes, UV linear absorption curves were recorded for 3 and 4, and comparatively studied with those of the boron-free π -systems NC-C₆H₄-C(H)=N-CH₃ (5) and NC-C₆H₄-C(H)=C(H)-C₆H₄-C(H)=N-CH₃ (6). The donor effect of the boron cluster was evidenced by a shift to the lower energy of the absorption band in the spectra of systems incorporating B₁₂. The two photon absorption (TPA) spectrum of compound 3, obtained by the up-conversion method, shows a resonance at 720 nm with a cross-section σ_{TPA} of 35 × 10⁻⁵⁰ cm⁴ s photon⁻¹ molecule⁻¹. This value suggests the potential of B₁₂ clusters to be used as new donor groups for the synthesis of non-linear materials.

Introduction

The dodecahydro-closo-dodecaborate dianion, [B₁₂H₁₂]²⁻, possesses the unique structure of a regular icosahedron and unique properties, such as high thermal stability, remarkable chemical and hydrolytical stability, and low toxicity. Since the isolation of $closo-[B_{12}H_{12}]^{2-}$ was first reported in 1960,¹ several routes to substituted closo-dodecaborate anions were envisaged via the formation of boron-nitrogen,^{2,3} -oxygen,^{4,-6} -sulfur,⁷ -halogen,⁸ -phosphorus⁹ or -carbon^{10,11} bonds. Their intrinsic properties make B₁₂-derivatives suitable for various possible applications, ranging from biomedical ones like boron neutron capture therapy (BNCT), a method for the treatment of cancer based upon the interaction of ¹⁰B atoms and thermal neutrons,¹² to the selective extraction of radionuclides from nuclear wastes arising from the PUREX process.13 The chemistry of closo-[B12H12]2-, together with the potential applications of its derivatives, was reviewed by Sivaev et al. in 2002.14

Despite the unique structure of closo- $[B_{12}H_{12}]^{2-}$, only little attention has been devoted to the optical properties of its derivatives. In 1999, Kaszynski *et al.* investigated the potentialities of closo- $[B_{12}H_{12}]^{2-}$ as building blocks for liquid crystal materials.¹⁵ Due to the variety of possible photonic applications, ranging from organic light-emitter diodes (OLEDs) for electroluminescence applications, to data storage, and optical switching and communications, another area of interest concerns the fabrication of second-order nonlinear optical (NLO) materials. In 2002, Marder *et al.* reviewed NLO and electrooptical (EO) materials containing boron.^{16,17} While many efforts were devoted to the

† Electronic supplementary information (ESI) available: Synthesis of 5; fluorescence emission spectrum of MSB, 3 and 6; normalized fluorescence emission spectrum of MSB, 3 and 6. See http://dx.doi.org/10.1039/b504414f

preparation of "push-pull" or centrosymmetric systems containing three-coordinate boron atoms,16,18,19 relatively little work was directed towards the incorporation of 12-vertex clusters into π -systems. Within this field, the most interesting results are large first hyperpolarizability (β) values calculated or measured for some derivatives of 12-vertex analogues of $closo-[B_{12}H_{12}]^{2-}$, namely the 1-carba-closo-dodecaborate anion, [CB11H12]-,20 and ortho-, meta- or para-carborane, $C_2B_{10}H_{12}$.²¹⁻²⁴ Besides secondorder NLO, the two-photon absorption (TPA) process is a three-order NLO process in which materials simultaneously absorb two photons. Materials exhibiting a large two-photon cross section and excellent up-conversion properties can find applications in various domains, like optical limiting,25,26 threedimensional optical data storage,27 and microfabrication.28 To our knowledge, the TPA properties of *closo*- $[B_{12}H_{12}]^{2-}$ derivatives have never been studied. In this context, two kinds of π -systems can be envisaged: (i) centrosymmetric systems incorporating one B_{12} cluster at each end of the π -transmitter, and (ii) noncentrosymmetric systems incorporating only one B₁₂ cluster as the donor group. By considering the complexity of B_{12} chemistry, we first focused our attention on the synthesis and characterization of non-centrosymmetric π -conjugated systems incorporating closo-B₁₂ as potential candidates for the TPA process. The results concerning the investigation of some of their optical properties will also be discussed.

Results and discussion

Synthesis and characterization of non-centrosymmetric π -conjugated systems

The synthesis of the π -conjugated systems has been conducted *via* the formation of Schiff bases. For that purpose, we have used the useful general pathway proposed by Sivaev *et al.*²⁹

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Indeed, these authors have reported that the monoamino derivative of the *closo*-dodecaborate cluster, $[B_{12}H_{11}NH_3]^-$ (1), can react with various arylaldehydes, $R-C_6H_4$ -CHO, to give the corresponding B_{12} -containing Schiff bases, $[B_{12}H_{11}N(H)=C(H)-C_6H_4-R]^-$. Therefore, we have prepared a series of π -systems consisting of electron-rich B_{12} -clusters bonded to electronacceptor CN groups through π -bridges of various lengths, *i.e.* $[NC-C_6H_4-C(H)=N(H)-B_{12}H_{11}]^-$ (2), $[NC-C_6H_4-CH=CH-C_6H_4-C(H)=N(H)-B_{12}H_{11}]^-$ (2), $[NC-C_6H_4-CH=CH-C_6H_4-CH=CH-C_6H_4-C(H)=N(H)-B_{12}H_{11}]^-$ (4) (Scheme 1). These expected donor- π -acceptor (D- π -A) systems should be classified as type II chromophores.^{30,31} In order to evaluate the contribution of B_{12} -clusters to the optical properties of such π -systems, we have also prepared boron-free analogues of (2) and (3), *i.e.* NC-C_6H_4-CH=N-CH_3 (5)³² and H_3CN=CH-C_6H_4-CH=CH-C_6H_4-CH=CH-C_6H_4-CN (6) (Scheme 2).



The first element of the series, $[NC-C_6H_4-C(H)=N(H)-B_{12}H_{11}]^-$ (2), was prepared in 60% yield from $[B_{12}H_{11}NH_3]^-$ and 4-cyanobenzaldehyde, according to the procedure initially reported by Sivaev *et al.*²⁹ According to DSC analyses, 2 exhibits a thermal stability up to 248 °C. In the same way, NC-C₆H₄-C(H)=N-CH₃ (5), an organic analogue of 2 consisting of a methyl group in place of the B₁₂-vertex, was synthesized from 4-cyanobenzaldehyde and aqueous methylamine.³²

The preparation of the other elements of the series was driven by the idea of increasing the length of their π -bridges, which is known to improve the two-photon absorption properties of the organic D– π -A systems.^{33,34} The synthesis of [NC–C₆H₄– CH=CH–C₆H₄–C(H)=N(H)–B₁₂H₁₁]⁻ (**3**) was conducted in three steps. First, diethyl 4-cyanobenzylphosphonate was prepared from triethyl phosphite and 4-(bromomethyl)benzonitrile, following a procedure described by Kagan *et al.*³⁵ In a second step and in the presence of potassium hydroxide, the reaction of terephthaldehyde with diethyl 4-cyanobenzylphosphonate yielded 4-cyano-4'-formylstilbene (7) (Scheme 3).

This intermediate was fully characterized by ¹H and ¹³C NMR analysis, FTIR and elemental analysis. According to DSC analysis, compound 7 exhibits a high thermal stability with decomposition starting at 382 °C. In a third step, the reaction of the monoamino derivative of B_{12} with 7, and in the presence of a catalytic amount of sodium hydroxide, yielded [NC-C₆H₄-CH=CH-C₆H₄-C(H)=N(H)-B₁₂H₁₁]⁻ (3) in 60% yield (Scheme 4).



Compound 3 was fully characterized by multinuclear NMR analysis. The ¹¹B{¹H} NMR spectrum of **3** shows only two signals, which are a singlet at -3.58 ppm and an unresolved signal at -14.64 ppm with a relative intensity of 1 : 11. The singlet at -3.58 ppm is the only one to be unaffected by the proton coupling during 11B NMR analysis. It was thus attributed to the boron atom bearing the imino substituent, whereas the unresolved signal at -14.64 ppm is the result of the overlap of the signals featuring the boron atoms in equatorial (10B) and apical (1B) positions relative to the pendant group. The complete identification of the substituent was conducted by ¹H NMR analysis. Beside the broad and unresolved signals (2.0 to 0.2 ppm) characteristic of the hydrogen atoms linked to the cluster, and to the signals (0.87, 1.28, 1.51 and 3.02 ppm) featuring the tetrabutylammonium cation, two doublets were observed at 8.75 and 10.43 ppm. Consistent with the ¹H NMR data of 2, these signals were attributed to hydrogen atoms bonded to the carbon and nitrogen atom of the imino bond, respectively. The three signals at 7.77, 7.79 and 7.96 ppm were attributed to aromatic hydrogen atoms of the stilbene backbone. Consistent with the assumed structure for 3, the two doublets at 7.42 and 7.49 ppm were attributed to the two hydrogen atoms of the ethenyl bridge connecting the two phenyl rings of the stilbene. One should also note that the value of the coupling constant of the ethenyl hydrogen atoms (16.4 Hz) revealed that the stilbene exhibits an (E)-configuration. The structure of 3 deduced from the NMR data was undoubtedly confirmed by FAB-MS analysis with the observation of the molecular peak at m/z = 372. Behind its potentially interesting optical properties, compound



The DSC analysis of 3 reveals an unusual feature with the observation of a glass transition temperature at 89 °C followed by a thermal degradation starting at 260 °C. This result underlines the thermoplastic behavior of 3, and one direct consequence is the ability of the latter to be shaped after softening, allowing the formation of complex shapes of 3-based materials such as films, lenses, coatings, fibers, foams, etc. As an illustration, when heated at ~ 160 °C, pure 3-powder melts and has sufficient viscosity to allow the formation of a lens in a glass mold (Fig. 1). This result is of particular scientific and technologic importance since one limitation for the integration of molecular π -systems into usable devices is the difficulty of their large-scale and homogeneous incorporation into polymer or inorganic matrices, forming efficient hybrid materials. This difficulty should be bypassed by the direct processing of 3forming pure optically-active materials in complex shapes.



Fig. 1 Fabrication of a lens by softening a powder of 3 at ~ 160 °C.

The glass transition temperature of **3** should be related to the existence of weak intermolecular interactions in the bulk. The exact nature of these interactions is unknown and further work is clearly needed in order to understand this phenomenon, and notably the role played by the counter cation, $N(n-Bu)_4^+$.

As we found, the reaction of 7 with aqueous methylamine yielded $H_3C-N=CH-C_6H_4-CH=CH-C_6H_4-CN$ (6), the organic analogue of 3 exhibiting a methyl group in place of the B_{12} cluster (Scheme 5). This compound was fully characterized by FTIR, EA, and ¹H and ¹³C NMR analysis.

Following a similar strategy, the synthesis of $[NC-C_6H_4-CH=CH-C_6H_4-CH=CH-C_6H_4-CH=CH-C_6H_4-C(H)=N(H)-B_{12}H_{11}][N(n-Bu)_4], [4] [N(n-Bu)_4], was conducted in three steps. First,$ *p*-xylylene-bis(triphenylphosphonium chloride) (8) was synthesized from triphenylphosphine and*p*-xylylene dichloride.³⁷ In a second step,

the reaction of **8** with 4-cyanobenzaldehyde and then terephthalaldehyde gave, in the presence of NaOCH₃, (E,E)-4-(2-(4-(2-(4-cyanophenyl)ethenyl)phenyl)ethenyl)benzaldehyde (**9**) (Scheme 6). In a third step, the reaction of **9** with **1** yielded **4** (Scheme 7).

By comparing 3 and 4, the main feature is the lower yield obtained for the synthesis of the latter (8% in comparison to 60% in the case of 3). This could be related to the extremely low solubility of 9, and therefore of 4, in organic solvents which is assumed to be the limiting step for the formation of 4. Moreover, this low solubility, together with the small amount of 4 obtained, precluded many analyses of this compound and only high-resolution ¹³C and ¹H NMR analysis have been performed. The attribution of the different signals was allowed by ${}^{1}H{-}{}^{1}H$, 1H-13C and 13C-13C COSY NMR analyses. All the NMR data are consistent with the structure suggested for compound 4. The four hydrogen atoms of the two ethenyl groups appeared as two doublets with a coupling constant of 16.2 Hz, emphasizing the (E,E)-configuration of the styrylstilbene derivative. The small amount of 4 obtained and its low solubility precluded also any optical characterization for this compound, and therefore there was no need for an organic analogue of 4.

UV-VIS linear absorption spectra of non-centrosymmetric π -systems 2, 3, 5, and 6

In order to evaluate the two-photon absorption (TPA) properties of our compounds, we had to determine first the potential of the B_{12} -cluster as a donor group in such π -systems. For that purpose, the first results concerning the optical properties of our systems are deduced from their linear absorption curves. Only little information is reported in the literature concerning the UV-VIS absorption properties of *closo*-boranes. As we found, the UV-VIS absorption spectrum of the parent monoamino derivative, $[B_{12}H_{11}NH_3][NBu_4]$, $[1][NBu_4]$, did not show any absorption band in the range 220–500 nm. Fig. 2 shows the UV-VIS absorption curves in molar extinction of compounds 2, 3, 5, and 6 in the range 200–500 nm.

The spectrum of NC–C₆H₄–C(H)=N–CH₃ (**5**) exhibits a first intense absorption band centered at 256 nm ($\varepsilon_{max} = 23650 \text{ L} \text{mol}^{-1} \text{ cm}^{-1}$) and a second weak one at 290 nm ($\varepsilon_{max} = 2000 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$). This pattern is in good agreement with those reported for disubstituted benzene derivatives.³⁸ Basically, the linear absorption spectrum of benzene shows two intense absorption bands at 180 nm (the second primary band, $\varepsilon_{max} =$ 47000 L mol⁻¹ cm⁻¹) and at 203 nm (the first primary band, $\varepsilon_{max} =$ 7400 L mol⁻¹ cm⁻¹), together with a weak third one at 254 nm (secondary band, $\varepsilon_{max} = 204 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$). These three bands are related to the π electrons and are shifted to higher wavelengths



Scheme 6







Fig. 2 Linear absorption spectra for compounds 2, 3, 5, and 6 (acetonitrile solution).

(red shift) in the presence of substituents. The magnitude of these red-shifts depends of the nature of the substituents and on their position on the ring.^{38,39}

In the case of **5**, red-shifts, $\Delta\lambda$, of 53 nm and 36 nm have been measured for the first primary band and secondary band, respectively. These values are in the same range as those reported for the reference compound, 4-aminobenzonitrile (ABN).⁴⁰ Moreover, the relative intensity of the first primary and secondary bands of **5**, estimated by the measurement of their oscillator strengths (0.47 and 0.08, respectively), is close to that reported for ABN.

The spectrum corresponding to $[NC-C_6H_4-C(H)=N(H)-B_{12}H_{11}]^-$ (2), analogue of 5 but containing a B_{12} -cluster in place of the methyl group, shows two intense absorption bands at 328 nm and 255 nm. The evolution of the pattern from 2 to 5 corresponds to that obtained with disubstituted benzene derivatives when increasing the strength of the donor/acceptor substituents.³⁸ On this basis, we assume that the intense absorption band at 328 nm corresponds to the first primary absorption band. We assume that this band overlapped the secondary absorption one. As we found, the red-shift for the first primary absorption band is $\Delta\lambda = 125$ nm compared to benzene. Moreover, we attribute the intense band at 255 nm to the second primary absorption. This assumption is in good agreement with the works of Doub *et al.*,

who reported similar patterns and the systematic observation of the second primary absorption band since $\Delta \lambda > 51.5$ nm for the first primary one.³⁸

Therefore, the comparative study of the spectrum recorded with **2** and **5** clearly demonstrates the donor effect of the electronrich B₁₂-cluster. According to Doub *et al.*, the influence of the donor/acceptor couple (H)C=N(H)-B₁₂H₁₁^{-/}CN on the optical properties of the benzene ring is in the same range as $O^-/C(O)CH_3$.³⁸

The investigation of the solvatochromism for 2 was conducted by recording linear absorption curves into a series of solvent: CH₂Cl₂, CH₃CN and CH₃OH (Fig. 3).



Fig. 3 Solvatochromic behavior of **2** (CH₂Cl₂, $\lambda_{max} = 338$ nm; CH₃CN, $\lambda_{max} = 328$ nm; CH₃OH, $\lambda_{max} = 318$ nm).

Fig. 3 shows a blue shift of the first primary absorption band when increasing the polarity of the solvent. This result clearly indicates that **2** has a negative solvatochromic behavior. This effect should be related to a decrease in the solute dipole moment upon excitation *i.e.* between ground state and excited state.³⁰ Since similar effects are usually observed for zwitterionic compounds,^{30,41} this result should be correlated with the ionic nature of **2** with a partial compensation of the (2–) charge of the cluster by the nitrogen atom of the iminium group. Moreover, the band at 255 nm, which we attribute to the second primary absorption band, is unaffected by the nature of the solvent. This result confirms our assumption concerning the attribution of the bands, since the second primary absorption band is known to remain unaffected when varying the solvent.

The stilbene-like compound NC–C₆H₄–C(H)=C(H)–C₆H₄– C(H)=N–CH₃ (**6**) contains the same donor and acceptor groups as **5**. Its electronic spectrum (Fig. 2) shows two absorption band at 334 nm ($\varepsilon_{max} = 18540 \text{ L mol}^{-1} \text{ cm}^{-1}$) and 236 nm ($\varepsilon_{max} = 9080 \text{ L}$ mol⁻¹ cm⁻¹), consistently with the spectra reported for other stilbene derivatives.^{42,43} For instance, the parent *trans*-stilbene, C₆H₅–C(H)=C(H)–C₆H₅, exhibits two bands at 237 and 311 nm corresponding to $\pi \rightarrow \pi^*$ electronic transition. The red-shift of the band located at the lowest energy is due to the presence of donor and attractor groups bonded to the *trans*-stilbene core in *para* position.⁴⁴

The comparative study of **5** and **6** shows a strong red-shift of the absorption bands. This observation is consistent with the increase of the length of the π -bridge going from **5** to **6**, which is known to reduce the difference between HOMO and LUMO *via* (i) an increase in the number of electrons in the π -systems and (ii) a shift in the π - π * electronic transition to the lower energy.

The spectrum corresponding to compound **3** shows two absorption bands at 362 nm ($\varepsilon_{max} = 50601 \text{ L mol}^{-1} \text{ cm}^{-1}$) and 235 nm ($\varepsilon_{max} = 16930 \text{ L mol}^{-1} \text{ cm}^{-1}$). It appears therefore that the band located at the lowest energy exhibits a red-shift ($\Delta \lambda =$ 30 nm) compared to **6**. Consistent with the result described above, this red-shift confirms the donor effect of the B₁₂-cluster. Moreover, a negative solvatochromic behavior was observed for **3** with a shift in the intense band going from 360 nm in methanol, to 363 nm in acetonitrile, and to 370 nm in dichloromethane.

Two-photon absorption (TPA) properties of 2, 3 and 6

The fluorescence quantum yields of $[NC-C_6H_4-C(H)=N(H) B_{12}H_{11}$]⁻ $B_{12}H_{11}^{-}$ (3), and NC-C₆H₄-C(H)=C(H)-C₆H₄-C(H)=N-CH₃ (6) were determined from the fluorescence emission spectra using p-bis(o-methylstyryl)benzene (MSB) as a reference. The spectra were recorded using an excitation wavelength of 340 nm, with an optical density of 0.050. For compound 2, we did not detect any fluorescence. For compound 6, the measured fluorescence quantum yield is as low as 0.7%, which precluded any interest in further optical characterization for this compound. The intensity of fluorescence for compound 3 is 0.9% compared to MSB. This value is close to organic stilbene-like compounds containing strong donor and acceptor groups. Indeed, the quantum yield of fluorescence for 4-cyano-4'-methoxystilbene varies between 1% and 1.7%, depending on the solvent.⁴⁵ The TPA spectrum for compound 3 was obtained by up-conversion fluorescence measurments using a Nd:YAG pumped optical paramagnetic oscillator that produce 2.6 ns (full width at half maximum) in the range 550-650 nm and using a Ti:sapphire femtosecond laser in the range 700-800 nm (Fig. 4). The excitation beam is collimated over the cell length (5 mm). The fluorescence is collected at 90° of the excitation beam and focused into an optical fiber connected to a spectrometer. The TPA cross section is determined at 720 nm using MSB as a reference standard, for which $\sigma_{\text{TPA}} = 1.6 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$ molecule⁻¹.⁴⁶ One should note that the TPA spectrum obtained with the nanosecond laser beam (550-600 nm) is expressed in arbitrary units without any calibration. Indeed, this spectrum was just recorded to verify the decrease in σ_{TPA} for the lower wavelength.

The TPA spectrum of **3** shows a strong resonance at 720 nm with a cross section $\sigma_{\text{TPA}} = 35 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$. This resonance is about twice that of the one-photon spectrum (362 nm), consistent with previous results on "push–pull" dyes.³³ Moreover, this value is red-shifted compared to the one of the parent molecule (*E*)-stilbene (514 nm), and, at this wavelength, the corresponding σ_{TPA} is also larger (12 × 10⁻⁵⁰ cm⁴ s photon⁻¹



Fig. 4 Nanosecond and femtosecond TPA spectrum in the range 550–800 nm for 3 (acetonitrile solution, 5×10^{-3} M).

molecule⁻¹ for (*E*)-stilbene).⁴⁷ These results clearly point out the role played by the B_{12} cluster on the TPA properties of such π -systems.

Conclusion

We report on the synthesis of several non-centrosymmetric π -conjugated systems incorporating B₁₂ clusters. In particular, a stilbene-like derivative [NC–C₆H₄–C(H)=C(H)–C₆H₄–C(H)=N(H)–B₁₂H₁₁]⁻ (**3**) was prepared. Its characterization by DSC reveals a glass transition temperature, allowing the possible melt-shaping of **3** into various forms, as a lens for instance. The comparative study of the linear absorption of these boronbased systems compared to boron-free analogues emphasizes the potential of the electron-rich B₁₂ cluster as a donor group. The two photon absorption (TPA) of compound **3** was also investigated, and a cross section σ_{TPA} of 35 × 10⁻⁵⁰ cm⁴ s photon⁻¹ molecule⁻¹ was measured. Further work is in progress in order to incorporate B₁₂ clusters in more efficient organic backbones, and then to improve the 3rd order NLO properties of our compounds.

Experimental

General considerations

All reactions were carried out under an atmosphere of pure argon using vacuum-line and Schlenk techniques with solvents purified by standard methods.⁴⁸ $(Et_3NH)_2[B_{12}H_{12}]$ was purchased from KATCHEM Ltd., Prague, and used without further purification. ¹H-NMR spectra were recorded at 300 MHz or 500 MHz on a Bruker AM 300 or a Bruker DRX 500 spectrometer, respectively. ¹³C-NMR spectra were recorded at 75 MHz or 125 MHz on a Bruker AM 300 or a Bruker DRX 500 spectrometer, respectively. ¹¹B-NMR spectra were recorded on a Bruker AM 300 spectrometer at 96.29 MHz with Et₂O·BF₃ as external reference (positive values downfield). 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 μ L⁻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, 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 $[NC-C_6H_4-C(H)=N(H)-B_{12}H_{11}][N(n-Bu)_4]$, [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 Raash.² The synthesis of $[NC-C_6H_4-C(H)=N(H)-B_{12}H_{11}]^-(2)$ was conducted from 1 by following the procedure reported by Sivaev *et al.*²⁹ The DSC analysis of **2** shows a melting point at 241 °C followed by a strong exothermic effect starting at 248 °C.

Synthesis of $[NC-C_6H_4-CH=CH-C_6H_4-C(H)=N(H)-B_{12}H_{11}]-[N(n-Bu)_4], [3][N(n-Bu)_4]$

In a first step, diethyl p-cyanobenzylphosphonate was synthesized according to a procedure previously reported by Kagan et al.³⁵ In a second step, 4-cyano-4'-formylstilbene was prepared by the procedure described below, consistent with a patent deposited by Reinehr.⁴⁹ 1.87g (33 mmol) of potassium hydroxide was dissolved in 25 mL of methanol at 45 °C. The solution was cooled to 0 °C, and then 4.09g (31 mmol) of terephthalaldehyde were added. Then 6.9g (25 mmol) of diethyl pcyanobenzylphosphonate were added dropwise during 2 hours. The mixture was heated at 40 °C during 2 hours, and then allowed to cool to r.t. 10 mL of methanol were added and the solution was kept under stirring during 12 hours. A pale yellow precipitate was obtained and subsequently isolated by filtration. The ensuing solid was washed with 250 mL of methanol, yielding 4.89g (21.2 mmol, 85%) of 4-cyano-4'-formylstilbene (7). (Found: C, 82.8; N, 5.9; O, 6.5; H, 4.6%. 7 requires C, 82.4; N, 6.0; O, 6.9; H 4.7%); δ_H (CD₃CN, 300 MHz) 7.43 (s, 2H, HC=CH), 7.74 (s, 4H, C_6H_4), 7.83 (d, 2H, C_6H_4 , ${}^{3}J_{H-H} =$ 8.29), 7.96 (d, 2H, C_6H_4 , ${}^{3}J_{H-H} = 8.29$), 10.01 (s, 1H, CHO); $\delta_{\rm C}$ (CD₃CN, 75 MHz) 111.79 (1C, C_6 H₄), 119.16 (1C, C_6 H₄), 127.73 (4C, C₆H₄), 129.84 (1C, HC=CH), 130.47 (2C, C₆H₄), 131.22 (1C, HC=CH), 132.65 (2C, C₆H₄), 136.48 (1C, C₆H₄), 142.06 (1C, C_6H_4), 191 (1C, C=O); v_{max}/cm^{-1} 2215 (CN), 1687 (CHO) (KBr). DSC analysis: mp 210 °C; strong exothermic effect starting at 382 °C.

In a third step, 0.442g (1.0 mmol) of $[B_{12}H_{11}NH_3][NBu_4]$ and 0.183g (0.8 mmol) of 7 were dissolved in 30 mL of dichloromethane. A few drops of an aqueous solution of sodium hydroxide (5 wt%) were then added to the mixture. The reaction mixture was stirred overnight at r.t. The solvent was removed in vacuum and further purification was performed by chromatography on silicagel (NORMASIC 40 µm-60 µm, Aldrich) using a CH₃CN/CH₂Cl₂ (4 : 1) solution and yielded, after evaporation of the solvent in vacuum, 0.31g (0.5 mmol, 60%) Bu)₄], [**3**][N(n-Bu)₄]. $\delta_{\rm H}$ (CD₃CN, 300 MHz) 0.2–2.0 (unresolved, B-H), 0.87 (t, 12H, N-(CH₂)₃CH₃), 1.28 (m, 8H, N-(CH₂)₂-CH2-CH3), 1.51 (m, 8H, N-CH2-CH2-CH2-CH3), 3.02 (t, 8H, $N-CH_2-(CH_2)_2-CH_3$, 7.42 (d, 1H, HC=CH, ${}^{3}J_{H-H} = 16.39$ Hz), 7.49 (d, 1H, HC=CH), 7.77 (s, 4H, $NC-C_6H_4$), 7.79 (d, 2H, C_6H_4 , ${}^{3}J_{H-H} = 8.47$ Hz), 7.96 (d, 2H, C_6H_4), 8.75 (d, 1H, *H*C=NH, ${}^{3}J_{H-H} = 19.78$ Hz), 10.43 (d, 1H, HC=N*H*); δ_{C} (CD₃CN, 75 MHz) 12.23 (4C, N-(CH₂)₃CH₃), 18.76 (4C, N-(CH₂)₂-CH₂-CH₃), 23.73 (4C, N-CH₂-CH₂-CH₂-CH₃), 58.79 (4C, N-CH₂-(CH₂)₂-CH₃), 111.59 (1C, C₆H₄), 119.16 (1C, CN), 128.03 (4C, C₆H₄), 129.12 (1C, C₆H₄), 130.80 (1C, HC=CH), 131.53 (2C, C₆H₄ together with 1C, HC=CH), 131.64 (2C, C₆H₄ together with 1C, HC=CH), 133.18 (2C, C_6H_4), 141.59 (1C, C_6H_4), 143.99 (1C, C_6H_4)169.31 (1C, HC=NH); $\delta_{B\{H\}}$ (CD₃CN) -3.58 (s, 1B), -14.64 (u, 11B); v_{max} /cm⁻¹ 3286, 3248 (NH), 2487 (B–H), 2223 (CN), 1640 (C=N) (KBr); *m*/*z* (FAB⁻) 372 (M⁻); DSC analysis: $T_g = 89$ °C, strong exothermic effect starting at 260 °C.

Synthesis of NC-C₆H₄-CH=CH-C₆H₄-C(H)=N-CH₃ (6)

In a typical experiment, 0.220 g (1.0 mmol) of 7 were added to 6 mL of an aqueous solution of monomethylamine (40 wt%).

The suspension was stirred at r.t. overnight. The title compound was extracted from the methanol solution using diethyl ether. After evaporation of the solvent, the crude product was washed with 100 mL of water. Further recrystallization in diethyl ether yielded 0.123 g (0.5 mmol, 50%) of pure H₃CN=CHC₆H₄-CH=CH-C₆H₄-CN (**6**) (Found: C, 83.2; H, 6.3; N, 10.5%. **6** requires C, 82.9; H, 5.7; N, 11.4%); $\delta_{\rm H}$ (CD₃CN, 300 MHz) 3.41 (s, 3H, N-CH₃), 7.10 (d, 1H, HC=CH, ${}^{3}J_{\rm H-H}$ = 16.4), 7.74 (s, 4H, C₆H₄), 7.83 (d, 2H, C₆H₄), 7.96 (d, 2H, C₆H₄), 8.19 (s, 1H, N=CH-); $\delta_{\rm C}$ (CD₃CN, 75 MHz) 48.46 (1C, N-CH₃), 127.36 (4C, C₆H₄), 128.14 (1C, HC=CH), 128.65 (2C, C₆H₄), 131.92 (1C, HC=CH), 132.92 (2C, C₆H₄), 136.48 (1C, C₆H₄), 138.75 (1C, C₆H₄), 141.95 (1C, C₆H₄), 151.12 (1C, C₆H₄), 161.83 (1C, HC=N); $v_{\rm max}/{\rm cm^{-1}}$ 2215 (CN), 1640 (C=N) (KBr); DSC analysis: mp 146 °C.

Synthesis of $[NC-C_6H_4-CH=CH-C_6H_4-CH=CH-C_6H_4-C(H)=N(H)-B_{12}H_{11}][N(n-Bu)_4], [4][N(n-Bu)_4]$

In a first step, *p*-xylylene-bis(triphenylphosphonium chloride) (8) was synthesized from triphenylphosphine and *p*-xylylene dichloride, as described in the literature.³⁷ In a second step, 2.124 g (3.0 mmol) of *p*-xylylene-bis(triphenylphosphonium chloride) and 0.219 g (1.6 mmol) of 4-cyanobenzaldehyde were dissolved into 30 mL of freshly distilled ethanol. A solution of 0.187 g (3.5 mmol) of NaOCH₃ into 50 mL of ethanol was added dropwise. After 12 hours of stirring at r.t., 0.432 g (3.2 mmol) of terephthalaldehyde was added to the reaction mixture, and then a solution of 0.221 g (4.1 mmol) of NaOCH₃ in 50 mL of ethanol was added dropwise. The color of the solution turned to pale yellow and the mixture was kept under stirring at r.t. during 12 h. The reaction mixture was concentrated under vacuum, yielding a yellow precipitate which was filtered off. The precipitate was washed with a mixture water/ethanol (1:1). Further recrystallization in DMF yielded 0.201 g (0.6 mmol, 20%) of (E,E)-4-(2-(4-(2-(4-cyanophenyl)ethenyl)phenyl)ethenyl)benzaldehyde (9). $\delta_{\rm H}$ (CD₃CN, 300 MHz) 7.18 (m, 4H, HC=CH), 7.50–7.60 (m, 8H, C₆H₄), 7.63 (d, 2H, C₆H₄), 7.81 (d, 2H, C₆H₄), 10 (s, 1H, -CHO).

In a third step, 0.107 g (0.32 mmol) of 9 and 0.262 g (6.54 mmol) of 1 were dissolved in 20 mL of DMF. The pH of the solution was adjusted to 9-10 by adding a few drops of aqueous sodium hydroxide (5 wt%). The color of the solution turned to orange. The mixture was kept under stirring at r.t. during 24 hours. Then DMF was evacuated under vacuum. Further purification was performed by chromatography on silicagel (NORMASIC 40 µm-60 µm, Aldrich) using CH_2Cl_2 then a CH_3CN/CH_2Cl_2 (1 : 4) solution and yielded, after evaporation of the solvent in vacuum, 18 mg (0.025 mmol, 8%) of pure [NC- C_6H_4 -CH=CH- C_6H_4 - $CH=CH-C_6H_4-C(H)=N(H)-B_{12}H_{11}[N(n-Bu)_4], [4][N(n-Bu)_4].$ $\delta_{\rm H}$ (DMSO, 500 MHz) 0.2–2.0 (*u*, B–*H*), 0.98 (t, 12H, N– (CH₂)₃₃), 1.38 (m, 8H, N-(CH₂)₂-CH₂-CH₃), 1.65 (m, 8H, N-CH2-CH2-CH2-CH3), 3.12 (t, 8H, N-CH2-(CH2)2-CH3), 7.32 (d, 2H, HC=CH, ${}^{3}J_{H-H} = 16.2$ Hz), 7.59 (d, 2H, HC=CH), 7.65 (s, 4H, C₆ H_4), 7.83 (d, 4H, C₆ H_4 , ${}^{3}J_{H-H} = 8.28$ Hz), 7.94 (d, 4H, C_6H_4) 8.71 (d, 2H, HC=NH, ${}^{3}J_{H-H} = 19.59$ Hz), 10.34(d, 2H, HC=NH); $\delta_{\rm C}$ (DMSO, 125 MHz) 13.59 (4C, N-(CH₂)₃CH₃), 20.09 (4C, N-(CH₂)₂-CH₂-CH₃), 24.06 (4C, N-CH₂-CH₂-CH₂-CH₃), 59.02 (4C, N-CH₂-(CH₂)₂-CH₃), 110.50 (1C, C₆H₄), 119.16 (1C, CN), 123.01 (2C, C₆H₄), 126.92 $(2C, C_6H_4), 128.48 (4C, HC=CH), 129.18 (4C, C_6H_4), 132.50$ $(2C, C_6H_4), 134.75 (2C, C_6H_4), 134.88 (1C, C_6H_4), 140.01$ (2C, C₆H₄), 144.42 (1C, C₆H₄), 145.41 (1C, C₆H₄), 154.19 (1C, HC = NH).

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