Syntheses and properties of core-substituted naphthalene bisimides with aryl ethynyl or cyano groups[†]

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This paper reports the synthesis, the absorption and the emission spectra and the electrochemical and spectroelectrochemical properties of new naphthalene bisimides substituted in positions 2 and 6 of the napthyl core by cyano, pyrrolidino, 4-phenylethynyl, 4-ethynyl-*N*,*N*-dihexylaniline or 4-cyanophenyl groups. The synthesis of these five new compounds shares the common precursor: 2,6-dibromonaphthalene tetracarboxylic dianhydride. We show that the aryl ethynyl substituent red-shifts the absorbance and enhances the fluorescence quantum yield of the naphthalene bisimide, making these new compounds potential useful dyes. The cyano groups directly connected to the naphthyl core significantly decrease the two first reduction potentials of the molecule. The large electron affinity and the stability of the radical anion of the latter compound make it ideally suited to transport electrons or to act as an electron acceptor.

1 Introduction

Naphthalene bisimides (NBI) are an important class of compounds because they have been used in many areas, such as molecular sensors,¹ light harvesting pigments,² organic semiconductors,^{3,4} photomolecular switches⁵ and the formation of hydrogen-bonded supramolecular assemblies.^{6,7} Naphthalene bisimide has also been used extensively by Wasielewski et al.8 and by other groups9,10 as an electron acceptor in molecular arrays for photoinduced electron transfer owing to its low reduction potential, its high-lying excited-state and the intense and well-defined spectroscopic signature of the radical anion.¹¹ It is known that there are anodes on the HOMO and LUMO orbitals at the imide nitrogen atoms.¹² Accordingly, the electronic properties of naphthalene bisimide are weakly affected by the substituents at the bisimide group. On the other hand, there are significant spin densities on the core of naphthalene to tune the electronic properties of NBI with substituents,^{2,7,12-14} but until recently the introduction of substituents on these positions required tedious and multi-step transformations.¹⁵ Very recently, Würthner's group¹⁴ and our group¹⁰ reported an efficient procedure to brominate in one step naphthalene tetracarboxylic dianhydride with dibromoisocyanuric acid. This strategy opens the way to easy functionalization of naphthalene bisimide core positions by various substituents. We report herein the synthesis and the characterization of a series of new naphthalene bisimide derivatives with interesting

optical and electronic properties which offer new possibilities of utilization for this class of compounds.

2 Experimental

General methods

¹H and ¹³C NMR spectra were recorded on a Bruker ARX 300 MHz or a Bruker AMX 400 MHz spectrometer. Chemical shifts for ¹H NMR spectra are referenced relative to residual protons in the deuterated solvent (CDCl₃ δ = 7.26 ppm). High resolution electrospray mass spectra (HR-ESIMS) were collected in positive mode on a MAT95XL from Thermo-finnigan. Matrix assisted laser desorption mass spectrometry analyses were performed on a Bruker Biflex III MALDI-TOF spectrometer using dithranol as matrix. The instrument was equipped with a nitrogen laser emitting at 337 nm, a 2 GHz sampling rate digitizer, a pulsed ion extraction source and a reflectron. Fourier transform infrared spectra were recorded in pressed KBr pellets on a Bruker Vector 22 spectrometer.

The electrochemical measurements were performed with a potentiostat-galvanostat MacLab model ML160 controlled by resident software (Echem v1.5.2 for Windows) using a conventional single-compartment three-electrode cell. The working electrode was a platinum disk of 4 mm² area, the auxiliary was a Pt wire and the reference electrode was the saturated potassium chloride calomel electrode (SCE). The supported electrolyte was 0.15 N Bu₄NPF₆ in dichloromethane and the solutions were purged with argon before the measurements. All potentials are quoted relative to SCE. In all of the experiments the scan rate was 100 mV s⁻¹ for the cyclic voltammetry and 15 Hz for pulse voltammetry. Spectroelectrochemical spectra were recorded in a thin quartz UV-visible cell (0.5 mm) surmounted with a reference electrode (SCE) and a platinum wire as counter electrode. The working electrode was a platinum grid inserted within the quartz cell and the other conditions are the same as those for the cyclic voltammetry. UV-visible absorption spectra were

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recorded on a UV-2401PC Shimadzu spectrophotometer. Fluorescence spectra were recorded on a SPEX Fluoromax fluorimeter and were corrected for the wavelength dependent response of the detector system (Hamamatsu R928). The fluorescence quantum yields were determined using 5,10,15,20-tetra(3,5-di-*tert*-butylphenyl)porphyrinato zinc(II) in DMF as standard and using $\phi_{\rm fluo} = 0.045$.¹⁶

Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with Merck 5735 Kieselgel $60F_{254}$. Column chromatography was carried out either with Merck 5735 Kieselgel 60F (0.040–0.063 mm mesh) or with SDS neutral alumina (0.05–0.2 mm mesh). Air sensitive reactions were carried out under argon in dry solvents and glassware. Chemicals were purchased from Aldrich or Acros and used as received. The solvents for the reactions were distilled prior to use following the standard purification procedures. 2,6-Dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisanhydride¹⁰ and 4-ethynyl-*N*,*N*-dihexylaniline¹⁷ were prepared according to previously reported procedures.

N,N'-Di-(2',6'-diisopropylphenyl)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (2)

2,6-Dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisanhydride **1** (601.6 mg, 1.41 mmol) was suspended in acetic acid (30 mL) and heated at reflux for 30 min. 2,6-Diisopropylaniline (1.6 mL, 8.47 mmol) was added and the mixture was kept at reflux at 120 °C for another 25 min. The solution was concentrated under vacuum and methanol (20 mL) was added to the remaining residue. The precipitated solid was filtered, washed with methanol and then with dichloromethane. The resulted solid was purified by silica gel column chromatography (CH₂Cl₂ : petroleum ether, 1 : 1) to give **2** as an orange solid (315.3 mg, 30%).

¹H NMR (300 MHz, CDCl₃): δ 9.12 (s, 2H), 7.53 (d, ${}^{3}J$ = 8.1 Hz, 1H), 7.51 (d, ${}^{3}J$ = 7.5 Hz, 1H), 7.36 (d, ${}^{3}J$ = 7.8 Hz, 4H), 2.65 (sept., ${}^{3}J$ = 6.9 Hz, 4H), 1.17 (d, ${}^{3}J$ = 6.9 Hz, 24H). ¹³C NMR (75 MHz, CDCl₃): δ 160.9, 160.8, 145.3, 139.5, 130.1, 129.8, 129.0, 128.6, 125.6, 124.3, 29.4, 23.9. IR (cm⁻¹): 3062, 2958, 2927, 2868, 1721, 1679, 1560, 1415, 1310, 1228, 719. MALDI-TOF: *m/z*: calcd C₃₈H₃₆Br₂N₂O₄ = 742.1; found 743.5 [M + H]⁺.

N,*N*'-Di-(2',6'-diisopropylphenyl)-2,6-bis{2[4-(dihexylamino) phenyl]ethynyl}naphthalene-1,4,5,8-tetracarboxylic acid bisimide (3)

Under a nitrogen atmosphere N,N'-di-(2',6'-diisopropylphenyl)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide **2** (31.9 mg, 0.043 mmol), Pd(PPh₃)₄ (4.9 mg, 4.28 µmol) and CuI (0.6 mg, 3.42 µmol) were dissolved in a previously degassed mixture of dry THF (4 ml) and triethylamine (4 ml). 4-Ethynyl-N,N-dihexylaniline (37.8 mg, 0.132 mmol) was added and the solution was stirred at 37 °C for 16 h. The solvents were removed under vacuum and the crude product was purified by silica gel column chromatography (CH₂Cl₂ : petroleum ether, 1 : 1) to give **3** as a blue solid (26.6 mg, 54%).

¹H NMR (300 MHz, CDCl₃): δ 8.90 (s, 2H), 7.56–7.50 (m, 6H), 7.38 (d, ³*J* = 7.5 Hz, 4H), 6.56 (d, ³*J* = 9.0 Hz, 4H), 3.28

(t, ${}^{3}J$ = 7.6 Hz, 8H), 2.75 (sept., ${}^{3}J$ = 6.9 Hz, 4H), 1.65–1.50 (m, 8H), 1.31 (broad s, 24H), 1.20 (d, ${}^{3}J$ = 6.6 Hz, 12H), 1.19 (d, ${}^{3}J$ = 6.9 Hz, 12H), 0.90 (t, ${}^{3}J$ = 6.4 Hz, 12H). ${}^{13}C$ NMR (75 MHz, CDCl₃): δ 162.6, 161.6, 149.2, 145.8, 137.5, 134.7, 130.8, 129.6, 127.8, 127.0, 124.6, 124.1, 123.6, 111.1, 107.8, 107.4, 90.5, 50.9, 31.6, 29.3, 27.2, 26.7, 24.0, 23.9, 22.6, 14.0. IR (cm⁻¹): 3074, 3032, 2958, 2926, 2867, 2172, 1710, 1672, 1603, 1568, 1520, 1218, 1190, 1158, 1132, 814. MALDI-TOF: *m/z*: calcd for C₇₈H₉₆N₄O₄ = 1152.7; found 1153.1 [M]⁺.

N,N'-Di-(2',6'-diisopropylphenyl)-2,6-bis(2-phenylethylenyl) naphthalene-1,4,5,8-tetracarboxylic acid bisimide (4)

Under a nitrogen atmosphere N,N'-di-(2',6'-diisopropylphenyl)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide **2** (30.4 mg, 0.041 mmol), Pd(PPh₃)₄ (4.7 mg, 4.08 µmol) and CuI (0.6 mg, 3.25 µmol) were dissolved in a previously degassed mixture of dry THF (4 mL) and triethylamine (4 mL). Phenylacetylene (22 µL, 0.20 mmol) was added and the solution was stirred at 35 °C for 1.5 h. The solvents were removed under vacuum and the residue was extracted with dichloromethane until the aqueous layer was neutral. The crude product was purified by flash silica gel column chromatography (CH₂Cl₂ : petroleum ether, 1 : 1) to give **4** as an orange solid (28.8 mg, 90%).

¹H NMR (300 MHz, CDCl₃): δ 9.01 (s, 2H), 7.68–7.65 (m, 4H), 7.56 (d, ${}^{3}J$ = 8.1 Hz, 1H), 7.53 (d, ${}^{3}J$ = 7.8 Hz, 1H), 7.40–7.36 (m, 10H), 2.75 (sept., ${}^{3}J$ = 6.9 Hz, 4H), 1.21 (d, ${}^{3}J$ = 6.6 Hz, 12H), 1.19 (d, ${}^{3}J$ = 6.9 Hz, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 162.2, 161.4, 145.7, 137.7, 132.7, 130.3, 129.9, 129.8, 128.5, 127.7, 127.4, 125.7, 125.4, 124.2, 122.3, 121.9, 103.6, 89.3, 29.4, 24.0, 23.9. IR (cm⁻¹): 3063, 2962, 2927, 2869, 2203, 1714, 1675, 1575, 1430, 1316, 1228, 1217, 753, 720, 687. MALDI-TOF: *m/z*: calcd for C₅₄H₄₆N₂O₄ = 786.3; found 786.8 [M]⁺.

N,*N*'-Di-(2',6'-diisopropylphenyl)-2,6-bis(4-cyanophenyl) naphthalene-1,4,5,8-tetracarboxylic acid bisimide (5)

Under a nitrogen atmosphere N,N'-di-(2',6'-diisopropylphenyl)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide **2** (30.4 mg, 0.041 mmol), Pd(PPh₃)₄ (2.4 mg, 2.04 µmol), Na₂CO₃ (17.3 mg, 0.163 mmol) and 4-cyanophenylboronic acid pinacol ester (37.4 mg, 0.163 mmol) were dissolved in a previously degassed mixture of ethanol (0.04 mL), toluene (0.24 mL) and water (0.11 mL). The solution was stirred at 56 °C for 16 h and then at 65 °C for 2 h. The solvents were removed under vacuum and the residue was extracted with dichloromethane. The crude product was purified by flash silica gel column chromatography (diethyl ether then CH₂Cl₂) to give **5** as a yellow solid (13.4 mg, 42%).

¹H NMR (300 MHz, CDCl₃): δ 8.74 (s, 2H), 7.73 (d, ³*J* = 8.4 Hz, 4H), 7.49 (d, ³*J* = 8.4 Hz, 4H), 7.44 (d, ³*J* = 8.1 Hz, 2H), 7.29 (d, ³*J* = 7.8 Hz, 4H), 2.67 (sept., ³*J* = 6.9 Hz, 4H), 1.16 (d, ³*J* = 6.6 Hz, 12H), 1.10 (d, ³*J* = 6.9 Hz, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 162.1, 146.4, 145.1, 144.6, 135.4, 132.2, 130.1, 129.6, 128.7, 128.3, 126.3, 124.3, 123.6, 118.4, 112.4, 29.4, 23.9, 23.8. IR (cm⁻¹): 3069, 2964, 2927, 2870, 2231, 1715, 1673, 1425, 1314, 1229, 717. MALDI-TOF: *m*/*z*: calcd for C₅₂H₄₄N₄O₄ = 788.3; found 789.8 [M + H]⁺.

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N,*N*'-Di-(2',6'-diisopropylphenyl)-2,6-bis(*N*-pyrrolidinyl) naphthalene-1,4,5,8-tetracarboxylic acid bisimide (6)

N,*N*'-Di-(2',6'-diisopropylphenyl)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide **2** (41.2 mg, 0.055 mmol) and pyrrolidine (2 mL) were stirred at 50 °C under a nitrogen atmosphere for 5 min. The excess of pyrrolidine was removed under vacuum and the residue was purified by flash silica gel column chromatography (CH₂Cl₂) to give **6** as a purple–blue solid (35.5 mg, 89%).

¹H NMR (300 MHz, CDCl₃): δ 8.44 (s, 2H), 7.50 (d, ³*J* = 8.4 Hz, 1H), 7.47 (d, ³*J* = 6.9 Hz, 1H), 7.33 (d, ³*J* = 7.5 Hz, 4H), 3.49 (broad t, ³*J* = 5.8 Hz, 8H), 2.75 (sept., ³*J* = 6.9 Hz, 4H), 2.01 (broad s, 8H), 1.17 (d, ³*J* = 6.6 Hz, 12H), 1.16 (d, ³*J* = 6.9 Hz, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 163.7, 161.8, 147.6, 145.8, 131.3, 129.4, 125.2, 123.9, 123.1, 121.9, 105.4, 52.7, 29.1, 25.8, 24.2, 23.7. IR (cm⁻¹): 3096, 3064, 3026, 2962, 2928, 2869, 1693, 1653, 1566, 1451, 1213. HRMS-ESI (*m*/*z*): calcd for C₄₆H₅₂N₄O₄ = 725.4067; found 725.4057.

N,*N*'-Di-(2',6'-diisopropylphenyl)-2,6-dicyanonaphthalene-1,4,5,8-tetracarboxylic acid bisimide (7)

N,N'-Di-(2',6'-diisopropylphenyl)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic acid bisimide **2** (37.2 mg, 0.05 mmol), zinc cyanide (46.9 mg, 0.40 mmol), 1,1'-bis(diphenylphosphino)ferrocene (3.9 mg, 7.03 µmol) and tris(dibenzylideneacetone) dipalladium(0) (7.2 mg, 6.99 µmol) were combined in dioxane (4 mL) and heated at reflux for 40 h under a nitrogen atmosphere. The crude product was diluted with dichloromethane, filtered through Celite, and the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography (CH₂Cl₂ : petroleum ether, 2 : 1) to give **7** as an orange–yellow solid (31.8 mg, 100%).

¹H NMR (300 MHz, CDCl₃): δ 9.18 (broad s, 2H), 7.56 (d, ³*J* = 8.1 Hz, 1H), 7.54 (d, ³*J* = 7.5 Hz, 1H), 7.37 (d, ³*J* = 8.1 Hz, 4H), 2.57 (sept., ³*J* = 6.9 Hz, 4H), 1.18 (d, ³*J* = 7.1 Hz, 12H), 1.16 (d, ³*J* = 7.1 Hz, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 159.8, 145.2, 136.6, 130.6, 128.7, 128.6, 128.4, 128.2, 127.5, 124.5, 117.5, 115.3, 29.7, 29.5, 24.0, 23.9. IR (cm⁻¹): 3070, 3031, 2964, 2927, 2869, 2231, 1724, 1684, 1442, 1314, 1231, 722. HRMS-ESI (*m*/*z*): calcd for C₄₀H₃₆N₄O₄ + Na⁺ 659.2634; found 659.2639.

3 Results and discussion

Synthesis

The preparation of the new compounds 2-7 is outlined in Scheme 1. The synthesis relies on the known 2,6-dibromonaphthalene tetracarboxylic dianhydride $1^{10,14}$ that was first reacted with 2,6-diisopropylaniline in acetic acid to afford the soluble 2,6-dibromonaphthalene bisimide 2.

Then, Sonogashira cross-coupling reaction of **2** with 4-ethynyl-N,N-dihexylaniline or with phenylacetylene under standard conditions gave respectively **3** and **4**. Suzuki cross-coupling was then applied to dibromo derivative **2** with 4-cyanophenylboronic pinacol diester, using Pd(Ph₃)₄ as catalyst and Na₂CO₃ as a base, to give the expected bis-coupled product **5** in 42% yield. The N,N-dipyrrolidino-naphthalene bisimide **6** was obtained by nucleophilic aromatic

substitution of the bromo group of **2** by pyrrolidine in 89% yield. Finally, the dicyanonaphthalene bisimide **7** was prepared in quantitative yield by palladium-catalyzed cyanation of the dibromonaphthalene bisimide **2** using zinc dicyanide following the method reported by Maligres and co-workers.¹⁸ These conditions were previously applied successfully by Wasielewski and coworkers for the preparation of cyano derivatives of perylene imide.¹⁹ All of the compounds are very soluble in dichloromethane and were characterized by ¹H, ¹³C NMR and IR spectroscopy and mass spectrometry.

UV-visible electronic absorption spectra

The ground-state optical absorption spectra of 2-7, recorded in dichloromethane, are shown in Fig. 1 and the spectroscopic data are gathered in Table 1.

As expected, the introduction of substituents on the naphthalene core led to significant changes of the absorption spectrum compared to the unsubstituted naphthalene bisimide (Fig. 1). The presence of the bromo or cyano substituents on the 2,6 positions of naphthalene bisimide does not shift significantly the maximum absorption of the π - π * transitions, but only affects the vibronic pattern of the S_0 to S_1 transition between 350-400 nm (Fig. 1). The fine vibronic structure of the unsubstituted naphthalene bisimide becomes more complex as a result of new vibronic modes being introduced by the substituents. The attachment of a phenyl ring by a carboncarbon σ bond on the naphthalene core (compound 5) partly restores the initial vibronic structure of the unsubstituted naphthalene bisimide and induces a slight bathochromic shift of the spectrum. This is certainly the consequence of a limited, but noticeable π -conjugation between the naphthalene and the phenyl.

The introduction of a triple bond between the naphthyl core and the phenyl ring (compound 4) alleviates the steric constraints of the ortho protons of the phenyl with those on the 3 and 7 positions and increases thereby the length of the π -conjugation. As a result, the narrowing of the HOMO-LUMO gap causes a red-shift of the π - π * transition by roughly 15 nm (0.76 eV). The presence of electron-rich substituents such as amino groups (compounds 3 and 6) shift the transitions to even lower energy. With reference to other works on perylene bisimide²⁰ and naphthalene bisimide^{12,14} derivatives, we attribute the new absorption band in the visible spectrum as an intramolecular charge transfer transition. This assignment is in agreement with the disappearance of this transition upon acidification with HPF₆, but which is restored upon addition of triethylamine (Figure S21, ESI[†]). The absorption spectrum of the protonated 3 is relatively similar to that of compound 4, indicating that once the amino groups are protonated they behave as electron-withdrawing groups and they do not significantly affect the UV-vis. spectrum (Figure S21, ESI[†]). In the push-pull compounds 3 and 6, the transition probably corresponds to a shift of electron density initially localized on the amino groups to the oxygen atoms of the bisimide groups. Interestingly, in compound 3 the charge transfer band is more red-shifted and more intense than that of compound 6 (Fig. 1). This is probably the consequence of a more extended π -conjugation that increases the magnitude



Scheme 1 Synthetic route for the preparation of the new naphthalene bisimides 3–7. *Reagents and conditions*: (*i*) 2,6-diisopropylaniline, acetic acid, reflux, 25 min, 30%; (*ii*) Zn(CN)₂, Pd₂(dba)₃, 1,1'-bis(diphenylphosphino)ferrocene, dioxane, reflux, 40 h, quant.; (*iii*) pyrrolidine, 50 °C, 5 min, 89%; (*iv*) Pd(PPh₃)₄, Et₃N, CuI, THF, phenylacetylene, 35 °C, 1.5 h, 90%; (*v*) Pd(PPh₃)₄, Et₃N, CuI, THF, 4-ethynyl-*N*,*N*-dihexylaniline, 37 °C, 16 h, 54%; (*vi*) Pd(PPh₃)₄, Na₂CO₃, 4-cyanophenylboronic acid pinacol ester, ethanol–toluene–water, 56 °C, 15 h, then 65 °C, 2 h, 42%.

of the dipolar transition owing to a longer charge transfer distance.

Emission spectroscopy study

The luminescence spectra of the new naphthalene bisimides 2–7 were recorded in dichloromethane. The emission quantum yield, the emission maxima and the 0–0 energy of the excited-states (E_{00}) are collected in Table 1.

Derivatives **4** and **6** are the only fluorescent compounds of the series (Figures S19 and S20, ESI†), whereas the naphthalene bisimides **5** and **7** substituted with cyano groups do not exhibit detectable fluorescence. The cyano derivative **7** behaves differently to the corresponding perylene imide derivative substituted with cyano groups, which shows a relatively high fluorescent quantum yield.¹⁹ The direct attachment of a phenyl ring to the naphthyl core significantly diminishes the fluorescence quantum yield. We also observed this phenomenon with a NBI derivative substituted with 4-phenylethynyl groups, therefore it may be the consequence of the intramolecular rotation of the phenyl unit with the naphthalene that lowers the radiative quantum yield. Interestingly, the fluorescence quantum yield of **4** has increased relative to **6** and to the unsubstituted NBI, and is higher than that of substituted NBI with primary amine.^{12,14} This underscores the benefit of the triple bond on the fluorescence quantum yield. It is noteworthy that the energy level of the singlet excited-state of these new compounds, although still high, has decreased compared to the unsubstituted naphthalene bisimide (Table 2).

Electrochemistry

To investigate the effects of the substituents of NBIs on the redox potentials, the new compounds were studied by cyclic voltammetry and the results are collated in Table 2. The cyclic voltammograms of compounds **2–7** are shown in Fig. 2.

All of the compounds exhibit two reversible reductions that are separated by about 500 mV. The compounds substituted





Fig. 1 Electronic absorption spectra of the naphthalene bisimides 2-7 along with that of *N*,*N'*-bis(octyl)-1,4,5,8-naphthalenetetracarboxylic acid bisimide (black dashed line) recorded in dichloromethane.

with electron-withdrawing groups such as 5 and 7 display anodically shifted reduction waves with an extremely positive reduction potential for the dicyano derivative 7

 $(E_{\text{Red1}} = +0.01 \text{ V vs. SCE})$. With such a low reduction potential, this latter molecule will certainly be useful as a final electron acceptor in molecular arrays for long-range electron transfer or for the development of materials exhibiting n-type conducting behaviour.⁴ Compared to the corresponding dicyano perylene diimide,¹⁹ compound 7 exhibits the same first reduction potential, whereas the second potential is cathodically shifted by circa 240 mV; this probably arises due to the smaller distance between the two negative charges localized on the oxygens of the bisimide groups. Although compound 5 also bears two cyano groups as in 7, the higher proximity of its redox potentials with those of 2, or of the unsubstituted NBI than those of 7, implies that there is limited communication through the phenyl group directly connected to the naphthalene core. In contrast, the presence of a triple bond enhances the electronic π -conjugation and induces a stabilization of the LUMO frontier molecular orbitals, thus rendering the molecule more reducible than the unsubstituted naphthalene bisimide. This is clearly observed in compound 3, substituted with the ethynyl N,N-dihexylamine group, which displays relatively accessible reduction potential in spite of the presence of electron-rich amino substituents. In compound 3, the high lying HOMO along with the stabilized LUMO explain the appearance of a low energy transition observed in the visible absorption spectrum.

Electron-releasing substituents such as the pyrrolidino group in 6 and the *N*,*N*-dihexylamino group in 3 destabilize the radical anion and shift the reduction processes to more negative regions, whereas the oxidation processes become more easily accessible (Table 2). For these two compounds, two reversible oxidation waves could be resolved within the electrochemical window of the solvent. Surprisingly, the first and the second oxidation processes are very close in compound 3, suggesting that the two positive charges are further away, so as to not interact with each other.

Table 1UV-vis. absorption and emission characteristics of compounds 2–7 recorded in dichloromethane. n.d. = not detected due to low emissionquantum yield (a) or emission wavelength outside the spectral window explored by our photodetector, e.g. $\lambda_{em} > 850$ nm (b)

Compound	$\lambda_{abs}/nm \ (\epsilon/mol^{-1} \ cm^{-1})$	$\lambda_{\rm em}/{\rm nm}$	$\phi_{\rm em}$	E_{00}/eV^{a}	
2	408 (1.65 \times 10 ⁴), 387 (1.46 \times 10 ⁴), 363 (2.45 \times 10 ⁴), 259 (6.79 \times 10 ⁴)	n.d. (a)	n.d. (a)		
3	$692(4.94 \times 10^{4}), 408(6.25 \times 10^{4}), 374(6.47 \times 10^{4}), 287(4.01 \times 10^{4})$	n.d. (b)	n.d. (b)		
4	$494(2.92 \times 10^{4}), 386(1.37 \times 10^{4}), 366(1.18 \times 10^{4}), 325(6.31 \times 10^{4})$	528	0.80%	2.35	
5	$379(1.77 \times 10^4), 255(4.41 \times 10^4)$	n.d. (a)	n.d. (a)		
6	$602(2.21 \times 10^4)$, $365(1.30 \times 10^4)$, $349(1.05 \times 10^4)$, $300(3.89 \times 10^4)$	623	0.20%	1.99	
7	$393(1.12 \times 10^4)$, $378(1.24 \times 10^4)$, $370(1.25 \times 10^4)$, $360(1.31 \times 10^4)$, $261(5.22 \times 10^4)$	n.d. (a)	n.d. (a)		
Unsubstituted NBI ^b	$382 (1.45 \times 10^4), 360 (1.15 \times 10^4), 343 (6.7 \times 10^3)$	387	0.16%	3.23	
$^{a}E_{00}$ was determined from the wavelength at the intersection of the absorption and the emission spectra. b Unsubstituted NN' -bis(octv)-1.4.5.8 naphthalenetetracarboxylic acid bisimide					

Table 2One-electron redox potential of the naphthalene bisimides 2–7 recorded in dichloromethane containing 0.15 M of Bu_4NPF_6 as supportingelectrolyte and referenced versus a saturated calomel electrode (SCE)

Compound	$E_{\text{Red2}}(\text{NBI}^-/\text{NBI}^{2-})$	$E_{\text{Redl}}(\text{NBI/NBI}^-)$	E _{Ox} (NBI ⁺ /NBI)	$E_{\rm Ox}({\rm NBI}^{2+}/{\rm NBI}^+)$
2	-0.96 V	-0.42 V	>1.6 V	
3	-1.00 V	-0.57 V	0.91 V	0.98 V
4	-0.96 V	-0.48 V	>1.6 V	
5	-0.96 V	-0.43 V	>1.6 V	
6	-1.36 V	-1.03 V	0.98 V	1.34 V
7	-0.62 V	0.01 V	>1.6 V	
Unsubstituted NBI ^a	-1.04 V	-0.64 V	>1.6 V	
^{<i>a</i>} Unsubstituted NBI = N	N'-bis(octvl)-1 4 5 8-naphthalenet	etracarboxylic acid bisimide.		



Fig. 2 Cathodic region of the cyclic voltammograms of compounds 2-7 recorded in dichloromethane containing 0.15 M of Bu₄NPF₆ as supporting electrolyte.

Spectro-electrochemical study

Transient UV–vis. spectra of compounds were recorded during electrolysis experiments and the maximum absorption wavelengths and the absorption coefficients of the new species that were formed are compiled in Table 3.

The stability of the radical anion of the compounds studied is demonstrated by the reversible recovery of the absorption spectrum of the initial neutral material by reversing the potential of the electrode. All of the electrochemical transformations gave rise to isosbestic points indicating the stepwise interconversion of one species into another (Fig. 3). In compounds **4**, **6** and **7** during the one-electron reduction, the initial strong absorption band in the visible decreases to leave new transitions at lower energies (Fig. 3). The second reduction of the dicyano derivative **7** is accompanied by new absorption bands, that are sufficiently distinct to those of the neutral and the radical monoanion to detect its formation by transient absorption spectroscopy. The spectral changes observed with reduction of **7** are in good agreement with those reported for the unsubstituted NBI.¹¹

Summary and conclusions

In this work, we have showed that the easily prepared dibromonaphthalene bisimide **1** is a reactive substrate in palladiumcatalyzed cross-couplings such as cyanation, Sonogashira and Suzuki reactions. We showed previously that the same compound could react smoothly with stannane in a Stille cross-coupling reaction according to classical conditions.¹⁰

The newly synthesized naphthalene bisimide derivatives were characterized by UV-vis. spectroscopy and we observed that the ethynyl substituted compound **4** is a soluble compound with a bathochromic absorption spectrum displaying an intense absorbance in the visible region and a relatively improved quantum yield compared to known NBI derivatives. A further shift to the near-infrared could be obtained by introducing electron donating groups on the ethynylphenyl substituents (compound **3**). This strategy could be useful, as it is envisioned to transform a poorly absorbing naphthalene bisimide molecule into a good chromophore in the visible spectrum. The coloured naphthalene bisimide dyes with absorption spectra spanning the solar spectrum could be

 Table 3
 Electronic absorption characteristics of the radical anions of the naphthalene derivatives measured in dichloromethane. The absorption coefficients were determined assuming complete conversion during electrolysis

Compound	$\lambda_{abs}/nm \ (\epsilon/mol^{-1} \ cm^{-1})$	
3-	839 (1.23 × 10 ⁴), 715 (1.88 × 10 ⁴), 670 (2.00 × 10 ⁴), 588 (1.58 × 10 ⁴), 518 (sh), 492 (2.81 × 10 ⁴), 431 (1.56 × 10 ⁴), 363 (4.16 × 10 ⁴)	
4-	832 (7.7 × 10 ³), 743 (1.19 × 10 ⁴), 634 (7.7 × 10 ³), 582 (1.03 × 10 ⁴), 540 (6.9 × 10 ³), 470 (2.07 × 10 ⁴), 324 (3.77 × 10 ⁴)	
6-	$687 (6.81 \times 10^4), 537 (sh), 506 (1.43 \times 10^4), 469 (8.2 \times 10^3), 282 (2.59 \times 10^4)$	
7-	770 (7.9 × 10 ³), 690 (4.1 × 10 ³), 608 (6.5 × 10 ³), 532 (1.2 × 10 ⁴), 490 (2.59 × 10 ⁴), 403 (6.9 × 10 ³), 381 (4.6 × 10 ³), 361 (3.7 × 10 ³), 306 (2.68 × 10 ⁴)	
7^{2-}	$600(1.26 \times 10^4), 549(9.0 \times 10^3), 509(4.8 \times 10^3), 459(4.23 \times 10^4), 432(2.15 \times 10^4), 294(2.38 \times 10^4)$	
Unsubstituted NBI ^a	755 (3.6 × 10 ³), 683 (2.1 × 10 ³), 605 (6.4 × 10 ³), 474 (2.30 × 10 ⁴)	
^{<i>a</i>} Unsubstituted NBI = N, N' -bis(oct	/l)-1,4,5,8-naphthalenetetracarboxylic acid bisimide from reference 11.	



Fig. 3 Time-resolved spectra of naphthalene bisimide derivatives 3, 4, 6 and 7 during reductive electrolysis recorded in dichloromethane containing 0.15 M of Bu_4NPF_6 as supporting electrolyte. The black bold trace is the initial spectrum and the red bold trace is the final spectrum. The arrows indicate the changes upon reduction.

valuable candidates for light harvesting systems. The electrochemical study showed that by varying the substituents on the core of naphthalene bisimides, it was possible to tune their reduction and oxidation potentials to a large extent.

A particular interest is the low redox potential of dicyano derivative 7, having a stable radical anion and dianion, making it a potential candidate as a mono and bi-electron acceptor for photoinduced electron transfer study or for use in the development of electron conductors. In view of its utilization as an electron acceptor, other noteworthy features of compound 7 are the high lying excited-state which precludes quenching by energy transfer and the marked and distinct spectroscopic signature of the radical monoanion and dianion that renders them easily detected by the classical transient spectroscopic experiments.

In conclusion, we have described the synthesis and the characterization of new attractive naphthalene bisimide derivatives with unusual optical and redox properties that are simple and cheap to prepare and that represent valuable molecules as dyes or electron acceptors.

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