

## NMP3-CT-2006-032636



# Delivery of new classes of materials, including characterization results



## EU Deliverable D4.4

Editors:	STRING WP4 members
Deliverable	EU Deliverable D4.4
Version:/ Status:	proposed
Date of issue:	October 15 <sup>th</sup> , 2009
Filename:	STRING_Del4.4_20091014_ab_v1.0.doc
Dissemination Level	Public

Project co-funded by the European Commission within the Sixth Framework Programme (2002-2006)

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## 0.2 DOCUMENT KEYDATA

Project Name & number	STRING, NMP3-CT-2006-032636
Deliverable nr	D4.4
Title of Deliverable	Delivery of new classes of materials, including characterization results
Contributing WP(s)	WP4
Dissemination level	PU: Public
Actual delivery date	October 15 <sup>th</sup> , 2009
Abstract:	In this document, the synthesis and photophysical characterization of a series of benzoxazole derivatives, acting as organic wavelelength shifters, is reported.

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## 1. Executive Summary

During the first four months of the project, WP4 partners have carried out an extensive literature survey, in order to spot the most promising classes of host matrix materials and organic luminescent converting dyes that can be utilized in a hybrid organic / inorganic scintillator stack. A list of key features required by these new materials has been drawn (see § 3.1 of D4.1). Following this work, some specific families of organic wavelength shifters that might be considered for our goals have been suggested; they include: *oligophenylenes*, *stilbenes*, *anthracenes*, *furans*, *oxazoles*, *oxadiazoles*, and *indoles* (see § 3.2 of D4.1). At the same time, quantum mechanical calculations focusing on a number of materials from the *stilbene*, *diphenyl acetylene*, and *diphenyl triazole* group have been performed, ending up with few design rules (see § 1 of D4.2). Accordingly, in the period ranging from M6 to M18 of the STRING project several new modified materials belonging to the classes of *oligophenilenes* emitters have been designed, synthesized and characterized for their photophysical properties in solution. The results of this investigation have been reported in EU Deliverable D4.2. Subsequently, the synthesized organic emitters have been embedded in solid state thin films and their photophysical behaviour have been studied and compared to that previously observed in solution (see EU Deliverable D4.3).

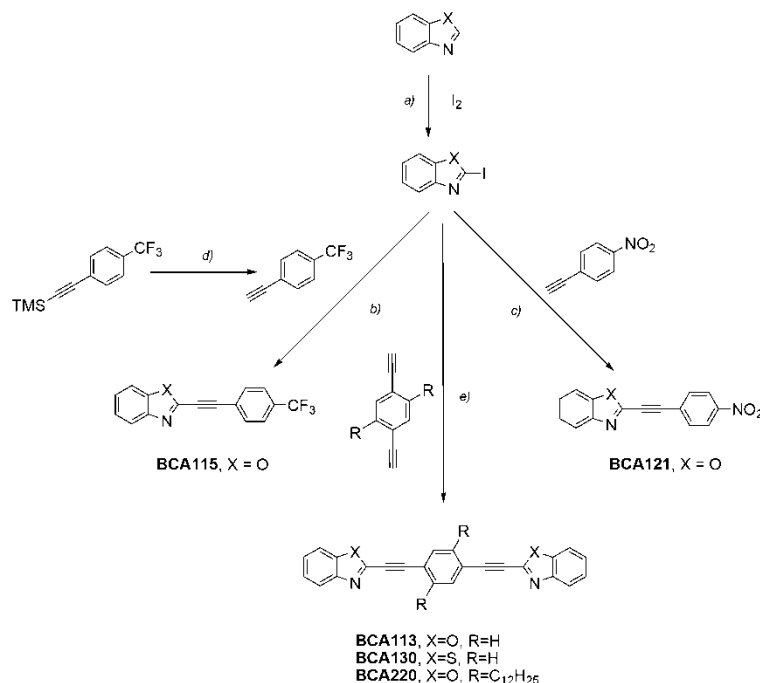
In the following subsections, a brief description and list of new materials prepared at CNR-ISOF and their photophysical characterization are reported. Results are collected in separate Material Data Sheets for each compound. The purpose of this report is to illustrate the progresses which have been achieved by the synthesis of a new set of organic fluorophores. The performances of this new linear benzoxazoles surpass those previously observed for oligophenilenes in term of their radiative constants by one order of magnitude and fit the purpose of the project.

## 2. General Synthetic Procedures

The synthetic strategy envisaged in order to build benzoxazole- and benzothiazole-based push-pull systems involves the employment of microwave assisted Sonogashira type reactions.<sup>2</sup> This method, in fact, allows us to decrease the reaction times of a normal Sonogashira reaction up to few minutes without strongly affecting the reaction yields.

The route towards benzoxazole- and benzothiazole-based molecules is outlined in Scheme 1. The synthetic pathway starts with the iodination of the commercially available benzoxazole and benzothiazole (Scheme 1, path a).<sup>3</sup> Subsequently, 2-iodobenzoxazole was coupled following microwave-assisted Pd(II)-catalyzed cross-coupling procedures, with 4-ethynyltrifluoromethylbenzene (Scheme 1, path b), and 4-ethynylnitrobenzene (Scheme 1, path c), giving the two targeted compounds **BCA115** and **BCA121** with satisfying yields (58% and 47% respectively).

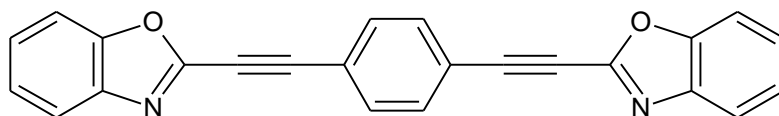
In addition, following a similar strategy the bisbenzoxazole and bisbenzothiazole derivatives **BCA113**, **BCA130**, were synthesized. Specifically, the 2-iodobenzoxazole intermediate formed in path a, reacted with 1,4-diethynylbenzene affording the desired molecule **BCA113** in 50% yield (Scheme 1, path e). With the same protocol, 2-iodobenzothiazole was coupled with 1,4-diethynylbenzene affording the targeted molecule **BCA130** in 58% yield (Scheme 1, path e). The poor solubility of compound **BCA113** in common organic solvents forced us in modifying its skeleton by introducing two long alkoxy chains as shown in compound **BCA220** (Scheme 1). Thus, 2-iodobenzoxazole intermediate reacted with 1,4-bis(dodecycloxy)-2,5-diethynylbenzene, synthesized as reported in literature,<sup>4</sup> in the presence of  $[\text{PdCl}_2(\text{PPh}_3)_2]$  and CuI in a mixture of  $i\text{Pr}_2\text{NH}$  and DMF obtaining the alkoxy derivatized bisbenzoxazole final compound **BCA220** in 30% yield (Scheme 1, path e).



a)  $\text{MgBr}_2\text{EtO}_2$ , BuLi, THF  $-10^\circ\text{C}$  14h; 54%. b) Microwave reaction:  $[\text{PdCl}_2(\text{PPh}_3)_2]$ , CuI,  $i\text{Pr}_2\text{NH}/\text{DMF}$   $80^\circ$  4min; 58%. c) Microwave reaction:  $[\text{PdCl}_2(\text{PPh}_3)_2]$ , CuI,  $i\text{Pr}_2\text{NH}/\text{DMF}$   $80^\circ$  8min; 47%. d) KOH, MeOH r.t. 30min; 97%. e) Microwave reactions:  $[\text{PdCl}_2(\text{PPh}_3)_2]$ , CuI,  $i\text{Pr}_2\text{NH}/\text{DMF}$   $80^\circ$  8min; < 50%.

**Scheme 1.** Synthesis of the benzoxazole derivatives.

## 2.1 1,4-bis-(benzoxazol-2-ylethynyl)benzene (BCA113)



### 2.1.1 Synthesis

To a microwave vial, 2-iodobenzoxazole (0.1 g, 0.4 mmol) and 1,4-diethynylbenzene (0.026 g, 0.2 mmol) in *i*Pr<sub>2</sub>NH (0.9 ml) and DMF (0.5 ml) were added. [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (5.6 mg, 0.008 mmol) and CuI (8 mg, 0.04 mmol) were added. The mixture was introduced in the microwave cavity for 5 min at 80°C. Upon completion, monitored by TLC (eluent: cyclohexane/AcOEt 9:1), the mixture was diluted with cyclohexane and a pale yellow precipitate obtained. The precipitate was filtered, washed with cyclohexane and recrystallized from hot cyclohexane affording pure **BCA113** (60 mg, 50%). Pale yellow powder. C<sub>24</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>, MW: 360.36 g/mol. Exact mass: 360.0899 g/mol. M.p. > 200°C.  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  3040.43s, 2927.22s, 2218.60m (-C≡C-), 1602.15m, 1551.05w, 1470.43m, 1446.16w, 1400.53m, 1338.7m, 1295.69m, 1236.55w, 1103.73w, 938.17w, 831.02w, 737.83w, 543.99s.  $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$  7.78 (dd,  $J_o$  6.6 Hz, 2H, ArH), 7.7 (s, 4H, ArH), 7.57 (dd,  $J_o$  6.6 Hz, 2H, ArH), 7.45-7.38 (m, 4H, ArH).  $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$  157.7, 141.9, 132.64 (C<sub>1</sub>, C<sub>2</sub> interpreted by HETCOR analysis), 126.73, 125.37, 120.9, 120.57, 110.9, 100.7, 92.7, 80.09. EI-MS m/z: 361 [*M*+1]<sup>+</sup>, 360 [*M*]<sup>+</sup>.

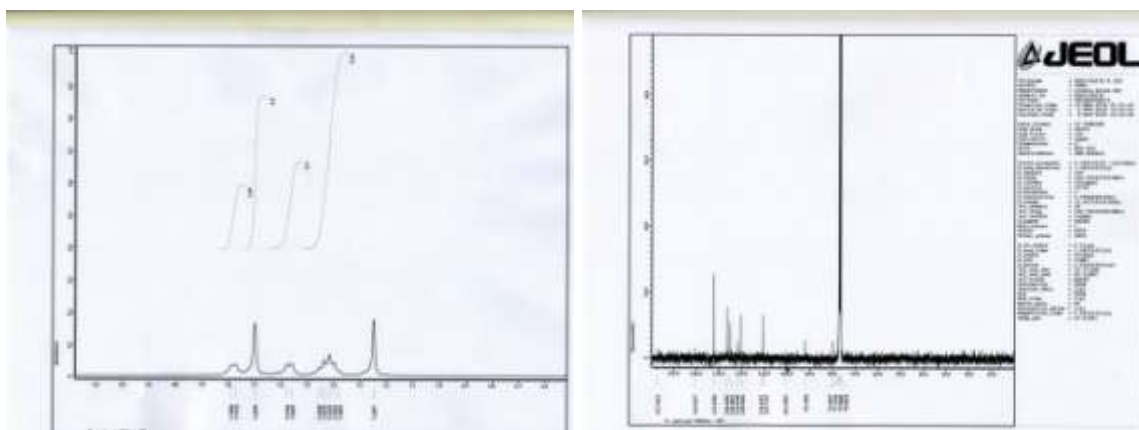


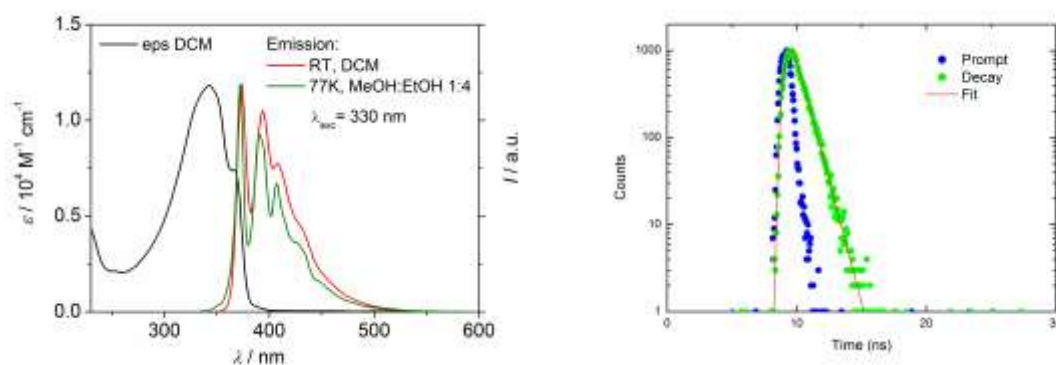
Figure 2.1.1. <sup>1</sup>H-NMR (left) and <sup>13</sup>C-NMR (right) spectra measured in CDCl<sub>3</sub> at room temperature.

## 2.1.2 Photophysics

**Table 2.1.2.** Photophysical parameters of **BCA113**.

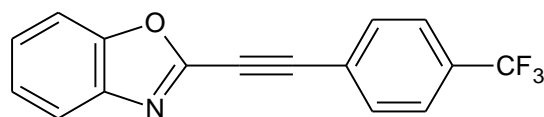
Solvent	Absorption (r.t.)		Emission (r.t.)			Emission (77 K) <sup>d</sup>	
	$\lambda_{max}$ (nm)	$\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{max}$ (nm) <sup>a</sup>	$\phi_{em}$ <sup>b</sup>	$\tau$ (ns) <sup>c</sup>	$\lambda_{max}$ (nm) <sup>a</sup>	$\tau$ (ns) <sup>c</sup>
TOL	344	14,100	374	0.75	0.75	372	0.63
	369	9,200	394				
			406 sh				
			426				
DCM	343	11,800	374	0.78	0.78	- <sup>e</sup>	- <sup>e</sup>
	367	7,400	394				
			408				

<sup>a</sup> Emission maxima derived from non-corrected emission spectra. Excitation at 330 nm. <sup>b</sup> Absolute quantum yields determined by comparing corrected emission spectra, using quinine sulfate in H<sub>2</sub>SO<sub>4</sub> 1 N as a standard.<sup>5</sup> Excitation at 330 nm. <sup>c</sup> Excitation at 331 nm. <sup>d</sup> In MeOH:EtOH 1:4. <sup>e</sup> No phosphorescence detected.



**Figure 2.1.2.** (left) Room temperature absorption (black line) and emission (red line) in dichloromethane; fluorescence (green line) at 77 K in MeOH:EtOH frozen glass mixture; excitation at 300 nm. Emission spectra are normalized to the intensity of the lowest energy absorption band. (right) Room temperature emission decay (green dots), excitation profile (blue dots) and mono-exponential fit (red line) of **BCA113** in dichloromethane solution; excitation at 331 nm.

## 2.2 2-[2-(4-trifluoromethylphenyl)ethynyl]-1,3-benzoxazole (BCA115)



### 2.2.1 Synthesis

To a microwave vial, 2-iodo-1,3-benzoxazole (0.2 g, 0.8 mmol) and 4-ethynyltrifluoromethylbenzene (0.2 g, 1.2 mmol) in *i*Pr<sub>2</sub>NH (1.8 ml) and DMF (1 ml) were added. [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (27 mg, 0.04 mmol) and CuI (14 mg, 0.078 mmol) were added. The mixture was introduced in the microwave cavity for 4 min at 80°C. Upon completion, monitored by TLC (eluents: cyclohexane/CH<sub>2</sub>Cl<sub>2</sub> 1:1), the mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with an aqueous soln. of HCl (0.1M). The residue was then purified by FCC (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane 1:1 up to 7:3) affording pure **BCA115** (130 mg, 58%). Pale yellow powder. C<sub>16</sub>H<sub>8</sub>F<sub>3</sub>NO, MW: 287.23 g/mol. Exact mass: 287.0558 g/mol. M.p.: 62-64°C.  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  3050.6s, 2921.83s, 2224.53m (-C≡C-), 1905.91s, 1779.56s, 1604.54m, 1549.54m, 1504.06s, 1477.09s, 1448.12m, 1404.97m, 1319.60w, 1239.44m, 1167.83w, 1123.33w, 1104.31w, 1065.14w, 1013.98m, 942.03m, 837.18w, 760.82w, 746.65w, 651.34s, 594.16m, 621.46s.  $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$  7.77 (m, 3H, ArH), 7.68 (d, 2H, F<sub>3</sub>C-ArH), 7.62 (d, 1H, ArH), 7.46-7.38 (m, 2H, ArH).  $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$  150.48, 147.22, 141.04, 132.83 (C<sub>3</sub>, C<sub>4</sub>, interpreted by HETCOR analysis), 126.81, 125.74, 125.70, 125.35, 124.01 (C<sub>1</sub>), 120.72, 110.83, 91.47, 79.9. EI-MS m/z: 288 [M+1]<sup>+</sup>, 287 [M]<sup>+</sup>.

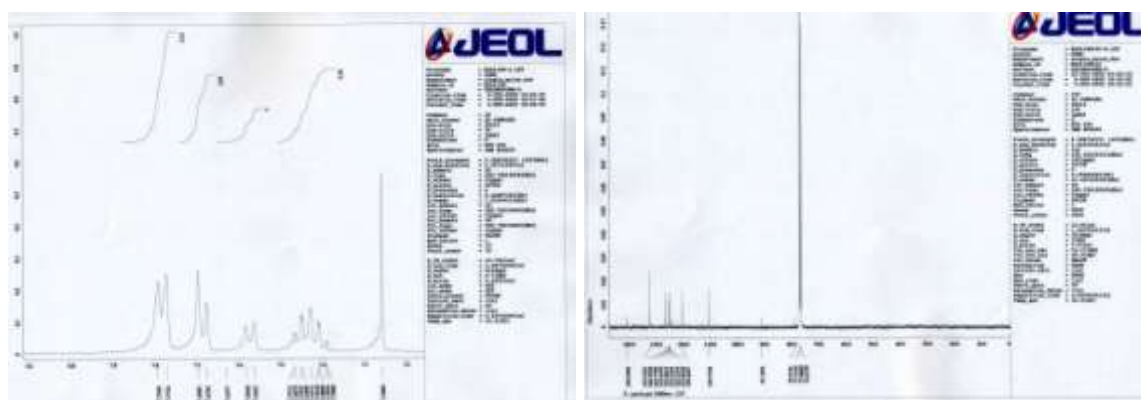


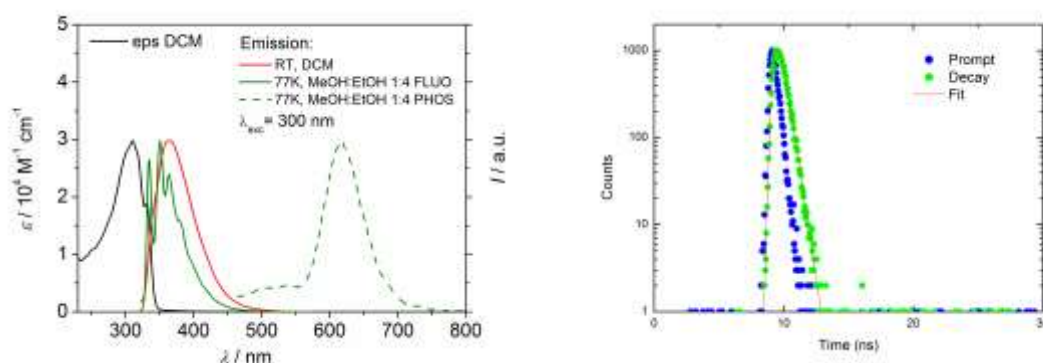
Figure 2.2.1. <sup>1</sup>H-NMR (left) and <sup>13</sup>C-NMR (right) spectra measured in CDCl<sub>3</sub> at room temperature.

## 2.2.2 Photophysics

**Table 2.2.** Photophysical parameters of **BCA115**.

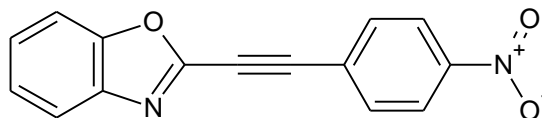
Solvent	Absorption (r.t.)		Emission (r.t.)			Emission (77 K) <sup>d</sup>	
	$\lambda_{max}$ (nm)	$\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{max}$ (nm) <sup>a</sup>	$\phi_{em}$ <sup>b</sup>	$\tau$ (ns) <sup>c</sup>	$\lambda_{max}$ (nm) <sup>a</sup>	$\tau$ (ns) <sup>c</sup>
TOL	312	28,700	363	0.26	0.47	335	0.91
	333	19,200				351	
DCM	310	29,800	363	0.21	0.39	364	380 sh
	331	18,900					
MeOH	308	31,900	364	0.15	0.36	617 <sup>e</sup>	0.25x10 <sup>6</sup> <sup>e</sup>
	328	19,600					

<sup>a</sup> Emission maxima derived from non-corrected emission spectra. Excitation at 300 nm. <sup>b</sup> Absolute quantum yields determined by comparing corrected emission spectra, using quinine sulfate in H<sub>2</sub>SO<sub>4</sub> 1 N as a standard.<sup>5</sup> Excitation at 300 nm. <sup>c</sup> Excitation at 278 nm. <sup>d</sup> In MeOH:EtOH 1:4. <sup>e</sup> Phosphorescence.



**Figure 2.2.2.** (left) Room temperature absorption (black line) and emission (red line) in dichloromethane; fluorescence (green line) and phosphorescence (green dashed line) at 77 K in MeOH:EtOH frozen glass mixture; excitation at 300 nm. Emission spectra are normalized to the intensity of the lowest energy absorption band. (right) Room temperature emission decay (green dots), excitation profile (blue dots) and mono-exponential fit (red line) of **BCA115** in dichloromethane solution; excitation at 278 nm.

## 2.3 2-[2-(4-nitrophenyl)ethynyl]-1,3-benzoxazole (BCA121)



### 2.3.1 Synthesis

To a microwave vial, 2-iodobenzoxazole (0.1 g, 0.4 mmol) and 4-ethynylnitrobenzene (70 mg, 0.4 mmol) in *i*Pr<sub>2</sub>NH (1.6 ml) and DMF (0.5 ml) were added. [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (14 mg, 0.02 mmol) and CuI (8 mg, 0.04 mmol) were added. The mixture was introduced in the microwave cavity for 8 min at 80°C. Upon completion, monitored by TLC (eluent: cyclohexane/CH<sub>2</sub>Cl<sub>2</sub> 1:1), the mixture was washed with cyclohexane and a pale yellow precipitate obtained. The precipitate was filtered, washed with cyclohexane and recrystallized from hot cyclohexane affording pure **BCA121** (50 mg, 47%). Pale yellow powder. C<sub>15</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>, MW: 264.23 g/mol. Exact mass: 264.0535 g/mol. M.p.: 130-132°C.  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  3105.72, 2360.21, 1591.96, 1520.15, 1343.5, 1305.53, 840.21, 765.2, 745.51.  $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$  8.29 (d, 2H, *J* 8.6, O<sub>2</sub>N-Ar), 7.84 (d, 2H, *J* 8.6, O<sub>2</sub>N-Ar), 7.8 (m, 1H, Ar), 7.58 (m, 1H, Ar), 7.49-7.4 (m, 2H, Ar).  $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$  148.28, 140.74, 133.28 (2C<sub>Ar</sub> interpreted by HETCOR analysis), 127, 126.85, 125.4, 123.9, 120.74, 110.8, 90.27, 81.6. EI-HRMS calc. 264.0535, *m/z*: 264.0531 ([M]<sup>+</sup> C<sub>15</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup>).

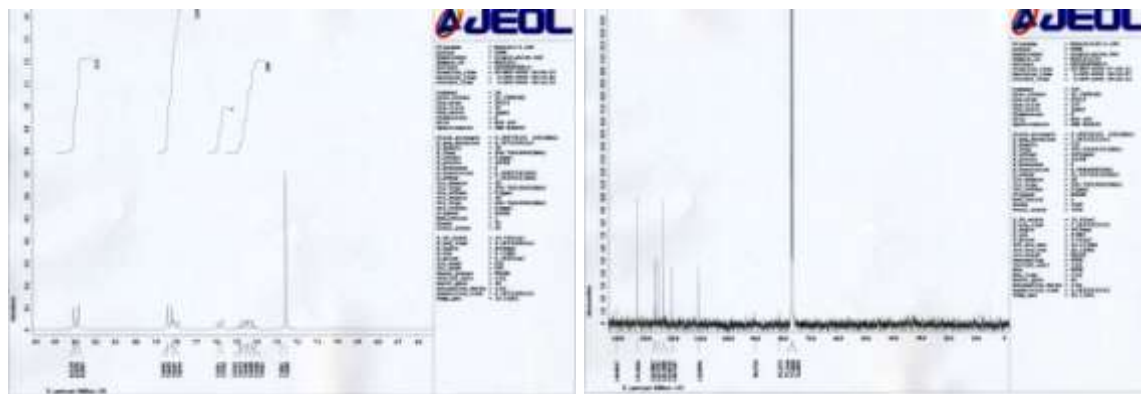


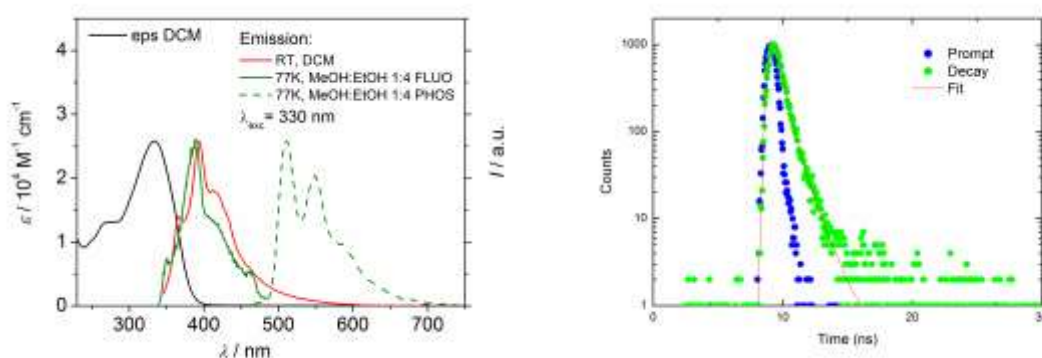
Figure 2.3.1. <sup>1</sup>H-NMR (left) and <sup>13</sup>C-NMR (right) spectra measured in CDCl<sub>3</sub> at room temperature.

## 2.3.2 Photophysics

**Table 2.3.** Photophysical parameters of **BCA121**.

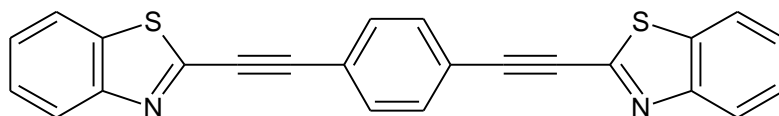
Solvent	Absorption (r.t.)		Emission (r.t.)			Emission (77 K) <sup>d</sup>	
	$\lambda_{max}$ (nm)	$\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{max}$ (nm) <sup>a</sup>	$\phi_{em}$ <sup>b</sup>	$\tau$ (ns) <sup>c</sup>	$\lambda_{max}$ (nm) <sup>a</sup>	$\tau$ (ns) <sup>c</sup>
TOL	335	24,900	365 394 416	$8.8 \times 10^{-4}$	0.34 1.5	389	1.0
DCM	334	25,800	366 393 412	$9.2 \times 10^{-4}$	0.33 1.0	511 <sup>e</sup> 549 585	$0.33 \times 10^9$ <sup>e</sup>
MeOH	-	-	363 390 412 sh	$7.1 \times 10^{-4}$	0.22 1.0		

<sup>a</sup> Emission maxima derived from non-corrected emission spectra. Excitation at 300 nm. <sup>b</sup> Absolute quantum yields determined by comparing corrected emission spectra, using quinine sulfate in H<sub>2</sub>SO<sub>4</sub> 1 N as a standard.<sup>5</sup> Excitation at 330 nm. <sup>c</sup> Excitation at 331 nm. <sup>d</sup> In MeOH:EtOH 1:4. <sup>e</sup> Phosphorescence.



**Figure 2.3.2.** (left) Room temperature absorption (black line) and emission (red line) in dichloromethane; fluorescence (green line) and phosphorescence (green dashed line) at 77 K in MeOH:EtOH frozen glass mixture; excitation at 330 nm. Emission spectra are normalized to the intensity of the lowest energy absorption band. (right) Room temperature emission decay (green dots), excitation profile (blue dots) and mono-exponential fit (red line) of **BCA121** in dichloromethane solution; excitation at 331 nm.

## 2.4 1,4-bis-(benzothiazol-2-ylethynyl)benzene (BCA130)



### 2.4.1 Synthesis

To a microwave vial, 2-iodobenzothiazole (0.1 g, 0.4 mmol) and 1,4-diethynylbenzene (0.025 g, 0.2 mmol) in *i*-Pr<sub>2</sub>NH (1.8 ml) and DMF (1 ml) were added. Subsequently, [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (5.5 mg, 0.008 mmol) and CuI (7 mg, 0.04 mmol) were added. The mixture was introduced in the microwave cavity for 4 min at 80°C. Upon completion, monitored by TLC (eluent: CH<sub>2</sub>Cl<sub>2</sub>), the mixture was diluted with cyclohexane and a pale yellow precipitate obtained. The precipitate was filtered, washed with cyclohexane and recrystallized from hot CH<sub>2</sub>Cl<sub>2</sub> affording pure **BCA130** (50 mg, 33%). Pale yellow powder. C<sub>24</sub>H<sub>12</sub>N<sub>2</sub>S<sub>2</sub>, MW: 392.5 g/mol. Exact mass: 392.0442 g/mol. M.p. > 200°C.  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  3051.21s, 2921.83s, 2223.40m (-C≡C-), 1604.02m, 1549.31w, 1476.81m, 1447.97w, 1404.9m, 1319.54w, 1167.5w, 1122.65w, 1103.77w, 1013.69w, 941.54w, 836.17w, 745.42w, 760.52w, 796.91s, 650.7s, 620.95s, 593.32m, 522.76s.  $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$  8.09 (d, *J*<sub>o</sub> 8 Hz, 2H, ArH), 7.89 (d, *J*<sub>o</sub> 8 Hz, 2H, ArH), 7.67 (s, 4H, ArH), 7.56-7.45 (m, 4H, ArH).  $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$  153.1, 141.2, 132.36 (C<sub>1</sub>, C<sub>2</sub> interpreted by HETCOR analysis), 126.95, 126.53, 123.87, 122.6, 121.47, 95.0, 89.6, 85.1. EI-MS *m/z*: 392 [M]<sup>+</sup>, 287 [M-(C<sub>6</sub>H<sub>5</sub>SH<sub>3</sub>)]<sup>+</sup>.

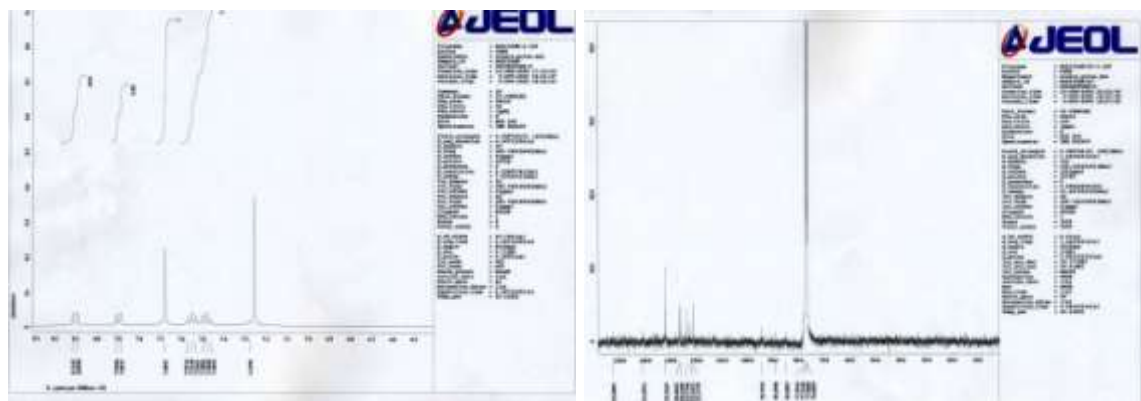


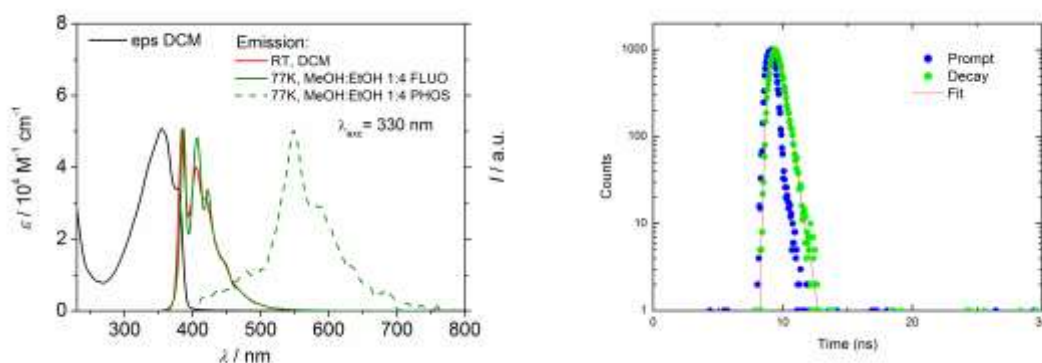
Figure 2.4.1. <sup>1</sup>H-NMR (left) and <sup>13</sup>C-NMR (right) spectra measured in CDCl<sub>3</sub> at room temperature.

## 2.4.2 Photophysics

**Table 2.4.** Photophysical parameters of **BCA130**.

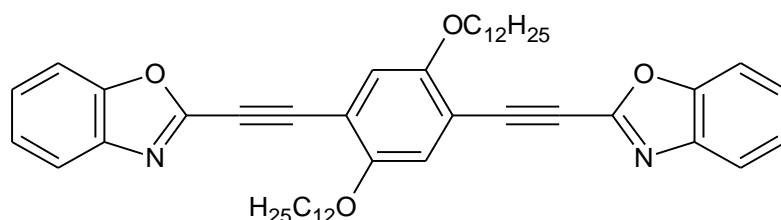
Solvent	Absorption (r.t.)		Emission (r.t.)			Emission (77 K) <sup>d</sup>	
	$\lambda_{max}$ (nm)	$\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{max}$ (nm) <sup>a</sup>	$\phi_{em}$ <sup>b</sup>	$\tau$ (ns) <sup>c</sup>	$\lambda_{max}$ (nm) <sup>a</sup>	$\tau$ (ns) <sup>c</sup>
TOL	355	37,000	384	0.50	0.40	387	0.53
	380	25,000	406				
			420				
DCM	355	51,000	384	0.42	0.39	549 <sup>e</sup>	9.5x10 <sup>6</sup> <sup>e</sup>
	378	34,000	406				
			418				
MeOH	-	-	382	0.53	0.39		
			402				
			416				

<sup>a</sup> Emission maxima derived from non-corrected emission spectra. Excitation at 330 nm. <sup>b</sup> Absolute quantum yields determined by comparing corrected emission spectra, using quinine sulfate in H<sub>2</sub>SO<sub>4</sub> 1 N as a standard.<sup>5</sup> Excitation at 330 nm. <sup>c</sup> Excitation at 331 nm. <sup>d</sup> In MeOH:EtOH 1:4. <sup>e</sup> Phosphorescence, weak signal.



**Figure 2.4.2.** (left) Room temperature absorption (black line) and emission (red line) in dichloromethane; fluorescence (green line) and phosphorescence (green dashed line) at 77 K in MeOH:EtOH frozen glass mixture; excitation at 250 nm. Emission spectra are normalized to the intensity of the lowest energy absorption band. (right) Room temperature emission decay (green dots), excitation profile (blue dots) and mono-exponential fit (red line) of **BCA130** in dichloromethane solution; excitation at 331 nm.

## 2.5 1,4-bis-(benzoxazol-2-ylethynyl)-2,5-didodecyloxybenzene (BCA220)



### 2.5.1 Synthesis

To a microwave vial, 1,4-bis(dodecyloxy)-2,5-diethynylbenzene (50 mg, 0.1 mmol) and 2-iodo-1,3-benzoxazole (50 mg, 0.2 mmol) in *i*-Pr<sub>2</sub>NH (0.5 ml) and DMF (0.5 ml) were added. Subsequently, [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (3 mg, 0.004 mmol) and CuI (4 mg, 0.02 mmol) were added. The mixture was introduced in the microwave cavity for 4 min at 80°C. Upon completion, monitored by TLC (eluents: cyclohexane/CH<sub>2</sub>Cl<sub>2</sub> 2:8), the formation of a yellow precipitate was observed. The precipitate was filtered, washed with cyclohexane and evaporated *in vacuo*. The residue was purified by FCC (SiO<sub>2</sub>; cyclohexane/CH<sub>2</sub>Cl<sub>2</sub> 2:8) affording pure **BCA220** (50 mg, 35%). Yellow powder. C<sub>48</sub>H<sub>60</sub>N<sub>2</sub>O<sub>4</sub>, MW: 729.0 g/mol. Exact mass: 728.4553 g/mol. M.p. > 200°C.  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  2923.51s, 2224.4m (-C≡C-), 1701.9w, 1553.53m, 1243.0m, 1220.4m, 938.17w, 1131.0w, 740.0s.  $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$  7.77 (dd,  $J_o$  1.8 Hz, 2H, ArH), 7.55 (dd,  $J_o$  1.8 Hz, 2H, ArH), 7.45-7.38 (m, 4H, ArH), 7.41 (s, 2H, ArH), 4.06 (t, 4H, OCH<sub>2</sub>), 1.89-1.85 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 1.55-1.53 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.29-1.23 (m, 32 H, CH<sub>2</sub>), 0.86 (t, 6H, CH<sub>3</sub>).  $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$  154.5, 150.24, 147.7, 141.17, 126.37, 125.04, 120.5, 117.37, 113.04, 110.62, 89.81, 83.1, 69.81, 31.9, 29.68, 29.61, 29.37, 29.34, 29.06, 27.87, 25.94, 22.68, 14.11.



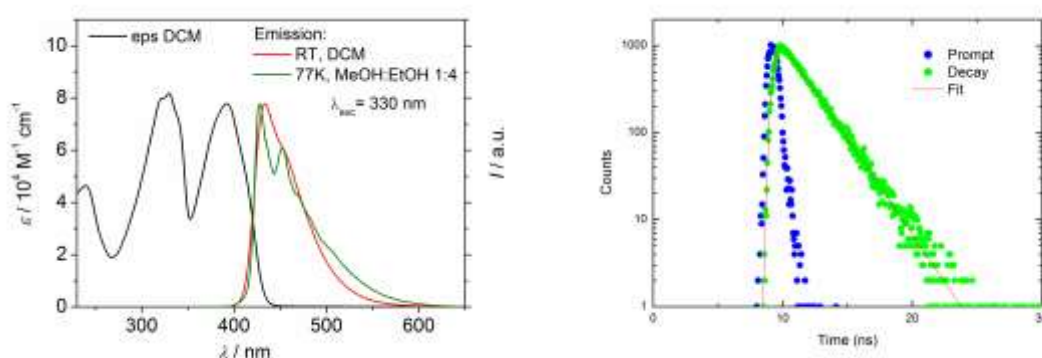
Figure 2.5.1. <sup>1</sup>H-NMR (left) and <sup>13</sup>C-NMR (right) spectra measured in CDCl<sub>3</sub> at room temperature.

## 2.5.2 Photophysics

**Table 2.5.2.** Photophysical parameters of **BCA220**.

Solvent	Absorption (r.t.)		Emission (r.t.)			Emission (77 K) <sup>d</sup>	
	$\lambda_{max}$ (nm)	$\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> )	$\lambda_{max}$ (nm) <sup>a</sup>	$\phi_{em}$ <sup>b</sup>	$\tau$ (ns) <sup>c</sup>	$\lambda_{max}$ (nm) <sup>a</sup>	$\tau$ (ns) <sup>c</sup>
TOL	331 394	79,000 78,000	430	0.75	1.7	428 452	1.7
DCM	330 392	82,000 78,000	434	0.79	2.0	- <sup>e</sup>	- <sup>e</sup>
MeOH	328 390	84,000 73,000	443	0.81	2.5		

<sup>a</sup> Emission maxima derived from non-corrected emission spectra. Excitation at 330 nm. <sup>b</sup> Absolute quantum yields determined by comparing corrected emission spectra, using quinine sulfate in H<sub>2</sub>SO<sub>4</sub> 1 N as a standard.<sup>5</sup> Excitation at 330 nm. <sup>c</sup> Excitation at 331 nm. <sup>d</sup> In MeOH:EtOH 1:4. <sup>e</sup> No phosphorescence detected.



**Figure 2.5.2.** (left) Room temperature absorption (black line) and emission (red line) in dichloromethane; fluorescence (green line) at 77 K in MeOH:EtOH frozen glass mixture; excitation 330 nm. Emission spectra are normalized to the intensity of the lowest energy absorption band. (right) Room temperature emission decay (green dots), excitation profile (blue dots) and mono-exponential fit (red line) of **BCA220** in dichloromethane solution; excitation at 331 nm.

## 3. Experimental Section

### 3.1 General Methods

Solvent and reagents were purchased as reagent-grade or better and used without further purification. All compounds were characterized by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR; IR; and HR-MS.  $^1\text{H}$  NMR spectra were recorded at 25 °C in  $\text{CDCl}_3$  on a 400 and 270 MHz JEOL instruments. Chemical shifts are reported in ppm downfield from  $\text{Me}_4\text{Si}$  using the residual solvent signals as an internal reference. Coupling constants ( $J$ ) are given in hertz. The IR spectra were collected with a Perkin-Elmer spectrometer RX-I FT-IR system, and the selected absorption bands are reported by wavenumber ( $\text{cm}^{-1}$ ). EI-HRMS and ESI-HRMS measurements were performed respectively on a  $\text{H}_2\text{O}$ s AutoSpec 6 F mass spectrometer and  $\text{H}_2\text{O}$ s QToF2 mass spectrometer both operating in positive mode. Microwave reactions were performed with a Biotage Initiator 2.0.

### 3.2 Optical Spectroscopy

Solution luminescence studies were carried out in spectrofluorimetric grade solvents. The absorption spectra of dilute solutions were obtained with a Perkin-Elmer Lambda 950 UV/Vis/NIR spectrophotometer. Molar absorptivity values ( $\epsilon$ ) were calculated applying the Lambert–Beer law to low absorbance spectra ( $A < 1$ ) of complexes recorded at successive dilutions.

The luminescence spectra were measured using a Spex Fluorolog II spectrofluorimeter, equipped with a Hamamatsu R928 phototube. Air-equilibrated sample solutions were excited at the indicated wavelength and the concentration was adjusted to obtain absorbance values  $A < 0.1$  at the excitation wavelengths. Uncorrected luminescence band maxima are used throughout the text, while corrected spectra were employed for the determination of the luminescence quantum yields ( $\phi$ ). The correction curve of the wavelength dependent phototube response between 280 and 900 nm has been obtained by using a calibrated halogen lamp source. Luminescence quantum efficiencies ( $\phi_{em}$ ) were evaluated using the method of Demas and Crosby<sup>6</sup> by comparing the wavelength integrated intensities ( $I$ ) with reference to a standard ( $\phi_r$ ) and by using the following equation:

$$\phi_{em} = \left(\frac{I \cdot n}{A}\right) \left(\frac{A_r}{I_r \cdot n_r}\right) \phi_r$$

where  $A$  and  $n$  are absorbance values ( $A < 0.15$ ) at the employed excitation wavelength and refractive index of the solvent, respectively. Band maxima and relative luminescence intensities are obtained with uncertainty of 2 nm and 20%, respectively.

The luminescence lifetimes were measured with an IBH 5000F time-correlated single-photon counting device, by using pulsed NanoLED excitation sources at 278 and 331 nm. Analysis of the luminescence decay profiles against time was accomplished with the Decay Analysis Software DAS6 provided by the manufacturer. Experimental uncertainties in the lifetime determinations are estimated to be 10%.

1 cm path-length square optical Suprasil Quartz (QS) cuvettes were used for measurements at room temperature of dilute solutions, while capillary tubes immersed in liquid nitrogen in a cold finger quartz dewar for measurements of MeOH–EtOH (1 : 4) frozen glasses at 77 K were used.

## 4. Concluding Remarks

In the present document the synthesis and photophysical characterization of a series of photoactive benzoxazolyl organic derivatives is reported. The photophysical properties have been investigated in solvents of different polarity and at different temperatures by steady-state absorption and emission spectroscopy, and by time-resolved luminescence.

Notably, the symmetric bis benzoxazole **BCA113** shows a high photoluminescence quantum yield coupled to a short lifetime of the excited state, thus resulting in a very high radiative constant ( $k_r \sim 10^9 \text{ s}^{-1}$ ). A phosphorescence emission is observed for the push-pull derivatives **BCA115** and **BCA121**, and for the symmetric benzothiazole **BCA130**. The insertion of alkyloxy lateral chains on the central phenyl ring of the symmetric bis-benzoxazole **BCA220** increased the solubility in alcohols, but had some effect on the emitting state.

A summary of the most valuable spectroscopic data for the fluorophores studied are collected in Table 4.1.

**Table 4.1.** Main photophysical parameters for the investigated compounds.

Compound	Absorption (r.t.) <sup>a</sup>		Emission (r.t.) <sup>a</sup>				Emission (77 K) <sup>b</sup>	
	$\lambda_{max}$ (nm)	$\epsilon$ ( $\text{M}^{-1} \text{cm}^{-1}$ )	$\lambda_{max}$ (nm)	$\phi_{em}$	$\tau$ (ns)	$k_r$ ( $\text{s}^{-1}$ )	$\lambda_{max}$ (nm)	$\tau$ (ns)
<b>BCA113</b>	343	11,800	374	0.78	0.78	$1.0 \times 10^9$	372	0.63
<b>BCA115</b>	310	29,800	363	0.21	0.39	$5.4 \times 10^8$	335	0.91
<b>BCA121</b>	334	25,800	366	$9 \times 10^{-4}$	0.33	$2.7 \times 10^6$	389	1.00
<b>BCA130</b>	355	51,000	384	0.42	0.39	$1.1 \times 10^9$	387	0.53
<b>BCA220</b>	392	78,000	434	0.79	2.00	$4.0 \times 10^8$	428	1.70

<sup>a</sup> In Dichloromethane. <sup>b</sup> In Methanol:Ethanol (1:4) mixture.

## 5. References

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