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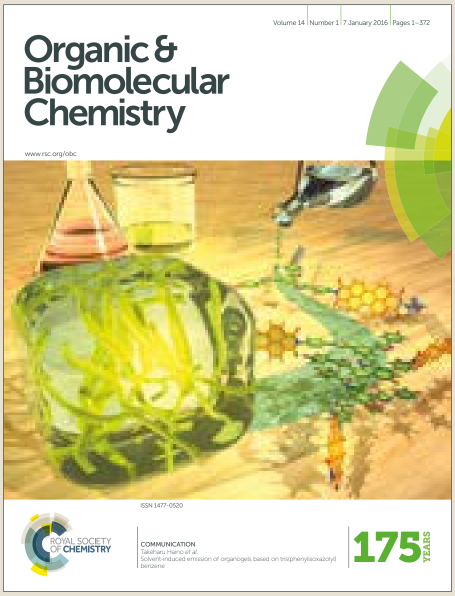

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Synthesis of Selectively 4-Substituted 9,9´-Spirobifluorenes and Modulation of Their Photophysical Properties.

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Synthesis of selectively 4-substituted 9,9’-spirobifluorenes was accomplished by using catalytic [2+2+2]-cyclotrimerization of specifically substituted diynols with alkynes to the corresponding fluorenols. Further synthetic transformations provided target molecules. Measurement of photophysical properties of the prepared 4-substituted 9,9’-spirobifluorenes revealed that emission maxima depended on electronic properties of the substituents present in the *para* position: the presence of electron accepting group strongly favored the maxima red shift toward the blue VIS region ($CF_3\lambda_{max}$ = 361 nm vs MeO λ_{max} = 330 nm). Adding further substituents (aryl or arylethynyl moieties) on the phenyl ring in the position 4 did not exert a dramatic improvement on the emission maxima ($CF_3C_6H_4$, λ_{max} = 369 nm, $CF_3C_6H_4C{\equiv}C$, λ_{max} = 370 nm), but increased considerably quantum yields. In addition, a series of 9,9’-spirobifluorenes possessing various extended π-systems (pyrene, anthracene, etc.) was synthesized. In general, the emission maxima pattern reflected that of the parent π-systems, but they were red shifted by 10~30 nm. Finally, also a 1-[4-(9,9'-spirobifluorene-4-yl)phenyl]-2-aryl-*ortho*-carborane was prepared. These data thus may provide guidelines for further design of 9,9’-spirobifluorenes with taylored properties. .

Introduction

Substituted 9,9’-spirobifluorenes have attracted considerable attention in material science due to their properties. They have been employed as interesting components for material chemistry in various applications, owing to their high thermal and morphological stability.[1] Studies concerning their electronic properties, especially for the application as electroluminescent layer in green and blue organic light emitting diodes (OLEDs), have appeared in the last decade,.[1b,2] In combination with other substances they can be used as well for white organic light emitting diodes (WOLEDs),[3] which are predicted to become the future of illumination systems.[4] However, it is still a challenge to develop blue light emitting materials with high efficiency by using short and high yielding syntheses. In addition, the blue OLEDs still lack in long operation times.[5] Pure hydrocarbon 9,9’-spirobifluorene materials were reported as a host for blue phosphorescent organic light emitting diodes (PhOLEDs).[6]

One of the possibilities to tune compound’s properties is to decorate it with either electron-withdrawing or -accepting functional groups or both in suitable positions on the molecule’s framework forming substances with push-pull characteristics. This has been exemplified in numerous examples in fluorene-type compounds.[7] Despite of this, a systematic study assessing electronic effects of various functional groups on photophysical properties fluorenes (and spirobifluorenes) has not been, to the best of our knowledge, pursued. Only recently (in 2017) a pioneering work in this respect has been reported and the results show that indeed the presence of electron rich or poor aromatic moieties in the position 4[8] or 3[9] of the fluorene skeleton can significantly change photophysical properties of the corresponding 9,9´-spirobifluorenes. These finding have been recently reviewed.[10] Since we have recently reported a new and efficient pathway for the synthesis of substituted 9,9´-spirobifluorenes based on a rhodium complex-catalyzed [2+2+2] cyclotrimerization as route for assembly of the substituted fluorene skeleton,[11] we envisioned that this methodology could provide a useful tool for preparation of series of specifically substituted fluorenes and 9,9´-spirobifluorenes possessing various substituents in the position 4. In this respect, we would like to report further developments in this area encompassing: a) a unified approach for the synthesis of series specifically substituted fluorenols in the position 4 of the fluorene framework and their conversion into the corresponding 9,9´-spirobifluorenes, b) progress in tuning of their photophysical properties utilizing electron donating and electron withdrawing substituents, as well as c) influence of the presence of extended π-aromatic hydrocarbon substituents and even carborane structures.

Results and discussion

Our choice of the starting material was at this point driven by ease of preparation **1** from a simple starting material as well as

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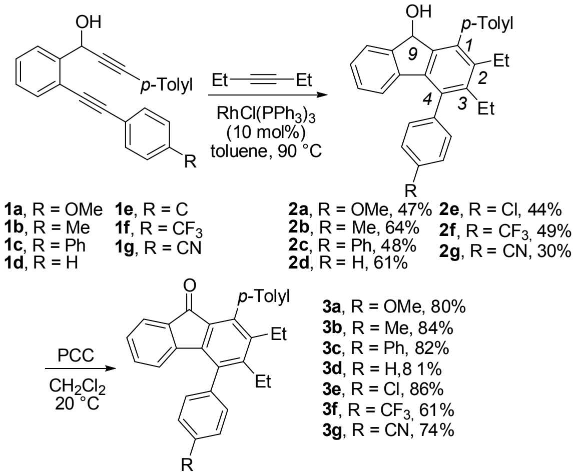
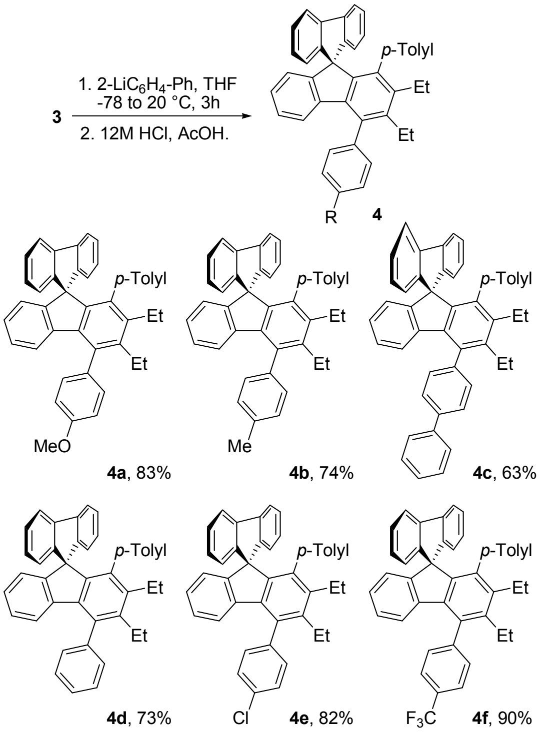
the fact that the presence of aryl or alkyl groups in the position 1 of the final 9,9´-spirobifluorenes does not have any significant influence on their photophysical properties, as it emerged from the previous studies of 1,2,3,4-tetrasubstituted 9,9’-spirobifluorenes.[11] The respective diynols **1a-1g** (Scheme 1) were prepared by using standard synthetic methodology based on Sonogashira coupling of 2-bromobenzaldehyde with various *para*-substituted phenylacetylenes bearing electron-donating (MeO, Me, H) and electron withdrawing (Ph, Cl, CF_3, and CN) groups followed by the subsequent alkynylation with *p*-tolylacetylide (for details, see SI). The prepared diynols **1** were cyclotrimerized with 3-hexyne in the presence of catalytic amount of Wilkinson’s catalyst ($RhCl(PPh_3)_3$, 10 mol%). In all cases the reaction proceeded successfully and the corresponding 4-substituted fluorenols **2a-2g** were isolated in reasonable yields (30-64%) (Scheme 1). With the series of substituted fluorenols **2** on hand, their oxidation with PCC in dichloromethane furnished the corresponding substituted fluorenones **3**. Also the oxidation proceeded uneventfully to provide the substituted fluorenones **3a-3g** in very good isolated yields (61-86%). These results provide evidence for a high functional group tolerance of the used methodology.



Scheme 1. Synthesis of fluorenones**3a-3g** from diynols**1a-1g**.

In the last step, fluorenones **3** were converted by a two-step method[12] into desired 9,9´-spirobifluorenes **4**. Thus addition of *ortho*-lithiumbiphenyl to fluorenones **3** gave rise to intermediate alcohols that were, without isolation, cyclized under acidic conditions into the corresponding 9,9´-spirobifluorenes **4a-4f** in sensible isolated yields in the range of 63-90% (Scheme 2). In the case of fluorenone **4g** the addition of *ortho*-lithiumbiphenyl proceeded preferentially to the CN group giving rise to an imine. Attempts to override this undesirable reaction by changing the reaction conditions were not successful.

The structures of selected 9,9´-spirobifluorenes were unequivocally confirmed by a single crystal X-ray structure analysis of **4a** (SI-Figure 1), **4c** (Figure 1) and **4e** (SI-Figure 1). The X-ray diffraction data revealed that in **4a**, **4c**, and **4e** the attached phenyl rings and the phenyl ring of the fluorene scaffold are almost perpendicular to each other with the angles of 86°, 94°, and 83°, respectively. These values are considerably more than those reported for the simple 4-phenyl-9,9´-spirobifluorene (~50°).[8b] It should be noted that an effect of the dihedral angle between the fluorene scaffold and the substituent in the position 4 on photophysical properties in the solid state has been recently observed.[13] There is no doubt that their almost perpendicular arrangement is the effect of a) the presence of the Et group in the *ortho* position of the phenyl linkage of the fluorenyl unit (C4) and b) the substituent in the *meta*-position (C3). Interestingly, no considerable deformation or twisting between the phenyl units of the fluorene scaffold was observed for **4a** (3.7°), **4c** (5.4°), and **4e** (2.1°).



Scheme 2. Synthesis of 9,9´-spirobifluorenes **4a-4f**.

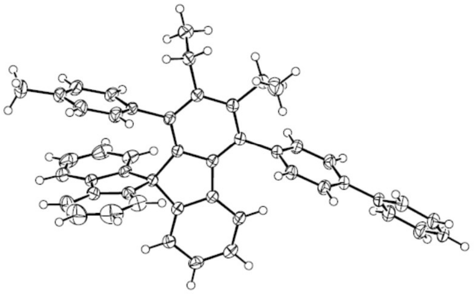


Figure 1. PLATON drawing of **4c** showing displacement ellipsoids on the 50% probability level.

Having the set of six differently substituted 9,9´-spirobifluorenes **4a-4f**, their photo-physical properties were

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studied. All measured compounds exhibited similar absorption spectral characteristics in the range of λ_{abs} = 250-330 nm, except of **4c** (possessing an additional biphenyl group), which shows a significant higher absorption in the area of 250-390 nm (Figure 2).The emission quantum yields (Φ_s) of these derivatives were determined in cyclohexane by the standard procedures with DPA as reference and were in an average range of Φ_s = 0.50-0.87 (Table 1 and Figure 2). The obtained emission maxima, ranged from 330 to 367 nm clearly indicating a relation between the emission of 9,9´-spirobifluorenes and the different R substituents. The plot of emission maxima versus the Hammett *para* substituent constants[14] σ_{para} indicates a reasonably good linear correlation for **4a**, **4b**, **4d-4f**. It is worth mentioning that introduction of the trifluoromethylphenyl group exerted red shift effect of 28 nm in comparison with the phenyl group. This value is more than twice larger than the one obtained for 2-pyridyl or 4-pyridyl groups, whose presence exerted the red shift of ~12 nm.[8c]

The only exception from linearity was observed for **4c**, featuring an unexpectedly high red shift of emission properties into the blue light region at λ_{em} = 367 nm (Figure 3) which is, undoubtly, an effect of the additional π-system (Ph). The obtained data allowed to conclude that the presence of electron deficient groups at the 4-position of the fluorene core bear a beneficial effect for red shift of emission maxima into the blue region. In a similar manner the results obtained with **4c** indicated that the presence of additional π-systems may result not only in higher shift to blue region but also increase quantum yield. In view aforementioned, it is reasonable to assume that the compounds **4** might undergo a stabilization of the excited state, e.g. a planarization of the structure, with the phenyl substituents conjugated to the spirofluorene core. This hypothesis is consistent with previously observed emission red-shift and for 4-aryl substituted spirobifluorenes.[8b,c] On the other hand, it should be noted that comparison of the emission maxima λ_{em} for **4d** (λ_{em} = 333 nm) and the parent 4-phenyl-9,9´-spirobifluorene (λ_{em} = 358 nm)[8b] indicates the blue shift for the former. This might be caused by the presence two ethyl groups in position 2 and 3. The blue shift is probably caused by a large dihedral angle and hence breaking of the π-conjugation between the substituent in the position 4 and the fluorene scaffold.[13]

Table 1. Photophysical properties for **4a-4f** (in cyclohexane).

Compound	λ_{abs}/nm (ε/10^4·mol^{-1}·dm^3·cm^{-1})	λ_{exc}/nm	λ_{em}/nm	Φ_s[a)]
4a	262 (sh), 269 (sh), 284 (sh), 300 (sh), 313 (1.6)	241	330	0.50
4b	262 (sh), 284 (sh), 300 (sh), 313 (1.6)	241	331	0.61
4c	250 (6.0), 255 (sh), 263 (sh), 284 (sh), 300 (sh), 313 (1.7)	243	367	0.87
4d	261 (sh), 284 (sh), 300 (sh), 313 (1.9)	242	333	0.66
4e	262 (sh), 284 (sh), 300 (sh), 313 (1.5)	241	344	0.61
4f	263 (sh), 274 (sh), 300 (sh), 313 (1.6)	240	361	0.64

[a)] Quantum yields were calculated relative to DPA (Φ_r = 0.97).

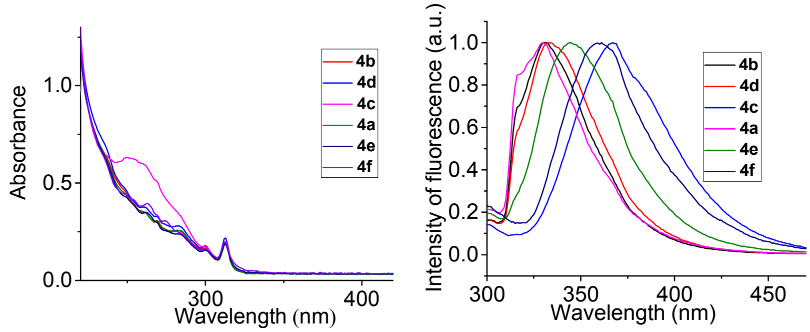

Figure 2. Absorption (left) and emission (right) spectra of **4a-4f**.

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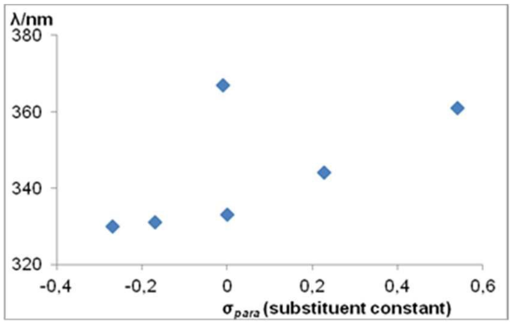
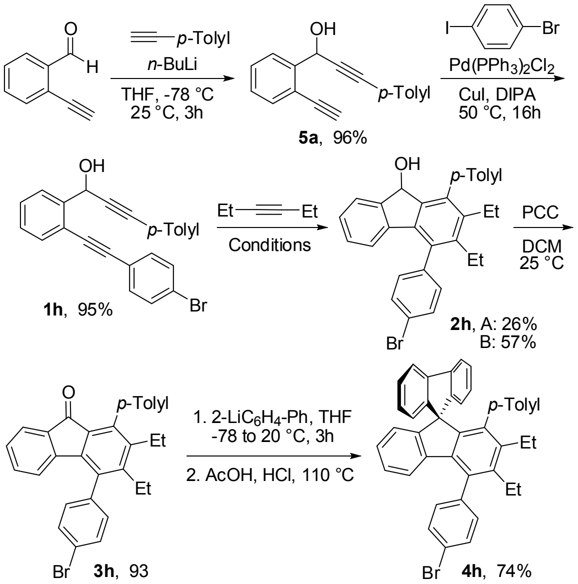


Figure 3. Plot of emission maxima versus Hammett substituent constant σ_{para}.

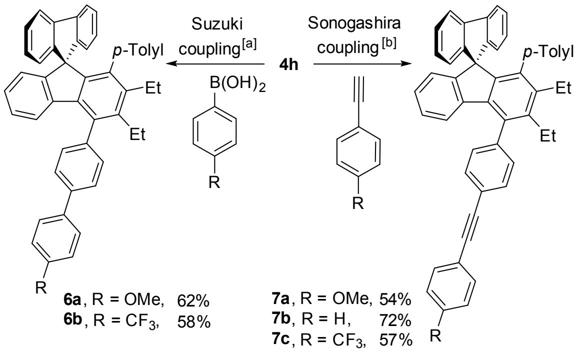
In view of the aforementioned and inspired by the unexpected behavior of **4c**, we decided to investigate the influence of extended π-systems at the 4-position of the fluorene skeleton. Thus we prepared 9,9′-spirobifluorene **4h** possessing the bromophenyl moiety as the convenient starting material for further attachment of other functional groups by using different cross coupling reactions. The diynol precursor **1h** was prepared by a modified standard procedure from **5a** in order to circumvent undesired homo coupling of 1-bromo-4-ethynylbenzene in Sonogashira coupling (Scheme 3). Unfortunately, cyclotrimerization of **1h** with 3-hexyne under the standard conditions (Condition A) furnished the desired fluorenol **2h** in only 26% isolated yield. Despite of the low yield, other possible products caused by Rh-catalyzed activation of the C-Br were not detected. This rather unsatisfactory result prompted us to try to tune reaction conditions using the Wilkinson's catalyst under modified reactions conditions. After considerable screening, it was found out that carrying out cyclotrimerization with $RhCl(PPh_3)_3$ (3 mol%) in the presence of a Ag-salt under microwave irradiation could deliver **2h** in almost double isolated yield of 57% (Condition B) (for details see SI-Table-1). Then **2h** was oxidized to **3h** in 93% isolated yield and the formation of spirobifluorene **4h** proceeded well giving 74% isolated yield (Scheme 3).

Having **4h** on hand, we started to extend conjugated π-system on the phenyl moiety in the position 4 by the use of Sonogashira or Suzuki coupling (Scheme 4). By using these cross coupling reactions we attached substituted phenylethynyl and phenyl groups to **4h** yielding the corresponding spirobifluorenes possessing substituted biphenyl **6a** and **6b** and substituted diphenylethynyl moieties **7a-7c** in generally acceptable isolated yields (54-72%). Structures of **6a** and **7b** (SI-Figure 2) were confirmed by a single crystal X-ray structure analysis. The X-ray diffraction data revealed that while for **6a** the angle between the mean plane of the attached phenyl rings and the phenyl ring of the fluorene scaffold are almost 90° to each other (83°), in case of **7b** the angle is only 75°. This arrangement is the result of the same effects as those observed for **4**. Also for **6a** and **7b** no considerable deformation or twisting between the phenyl units of the fluorene scaffold was observed being 5.7° and 4.8°.



Conditions A: $RhCl(PPh_3)_3$ (10 mol%), toluene, 90 °C, 16h.
Conditions B: $RhCl(PPh_3)_3$ (3 mol%), Ag_2CO_3, THF, MW, 180 °C, 1.5h.

Scheme 3. Synthesis of 9,9′-spirobifluorene **4h**.



[a] Conditions: $Pd(OAc)_2$ (5 mol%), K_2CO_3, $EtOH/H_2O$, 80°C, 3 h.
[b] For reaction conditions, see SI.

Scheme 4. Synthesis of extended 9,9′-spirobifluorenes **6** and **7**.

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Despite of the presences of the extended π-system and electron-accepting and, especially, electron-withdrawing groups, which had a beneficial effect on the red-shift towards the blue VIS region, these compounds, exhibited only negligible emission red shifts in comparison with **4c** (λ_{em} =367). emission maxima λ_{em} for **6a**, **6b**, **7a**, **7b**, and **7c** were observed at 366, 369, 367, 369, and 370 nm, respectively. The similar values indicate of λ_{em} that the effect of the pending aromatic side chains rather depends on the angle between the mean plane of the attached phenyl rings and the phenyl ring of the fluorene scaffold then extension of the p-system. Moreover, it should be taken into the account a preferential perpendicular rearrangement of the aromatic rings in the pendant chain that would contribute to breaking of the π-conjugation within the pendant chain. The emission quantum yields (Φ_s) of the derivatives were determined in cyclohexane by standard procedures with DPA as reference (Table 2 and Scheme 4). All samples possess high quantum yield of emission, especially **7c** with Φ_s = 1.00.

Table 2. Photophysical properties for **6**and **7**(in cyclohexane).

Compound	λ_{abs}/nm (ε/10^4·mol^{-1}·dm^3·cm^{-1})	λ_{exc}/nm	λ_{em}/nm	$\Phi_s$$^{a)}$
6a	216 (1.1), 264 (0.9), 284 (sh), 313 (sh)	254	366	0.65
6b	218 (1.1), 250 (sh), 261 (sh), 300 (sh)	251	369	0.99
7a	220 (1.4), 285 (sh), 296 (sh), 313 (sh)	253	367	0.82
7b	220 (1.6), 287 (sh), 305 (sh), 312 (sh), 328 (sh)	254	369	0.79
7c	220 (1.0), 252 (sh), 266 (sh), 276 (sh), 284 (sh), 291 (sh) 300 (sh), 312 (sh)	248	370	1.00

$^{a)}$ Quantum yields were calculated relative to DPA (Φ_r = 0.97).

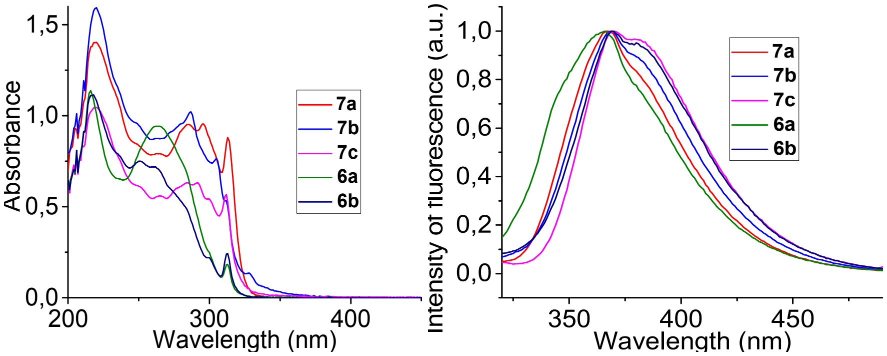

Figure 4. Absorption (left) and emission (right) spectra of **6**and **7**.

The above mentioned results indicating that attachment of rather simple aromatic substituents in the position 4 was sufficient to induce the shift of emission into the blue VIS region, prompted us to prepare derivatives with larger π-extended systems. In this respect as potential candidates appeared to be naphthyl, anthracenyl, phenanthrenyl, and pyrenyl moieties. In this instance synthesis of diynol precursors **8a-8d** (45-59% isolated yields) was carried out by using a slightly changed version of the previously developed general protocol, starting from 2-ethynylbenzaldehyde with addition of *n*-propynylacetylide followed by Sonogashira coupling with the corresponding aryl halides. The cyclotrimerization with 3-hexyne gave rise to the corresponding fluorenols **9a-9d** in good isolated yields (45-59%).

The subsequent oxidation with PCC in dichloromethane proceeded uneventfully as expected, providing **10a-10d** in good isolated yields (84-91%). Finally, the addition of *ortho*-lithiumbiphenyl followed by acidic treatment furnished 9,9´-spirobifluorenes **11a-11d** in good to high yields (51-91%, Scheme 6). The structure of **11b** was confirmed by a single crystal X-ray structure analysis (SI-Figure 2). The X-ray diffraction data revealed that for **11b** the angle between the mean plane of the attached phenyl rings and the phenyl ring of the fluorene scaffold are almost 91.8° and no considerable deformation or twisting between the phenyl units of the fluorene scaffold was observed being 0.1°.

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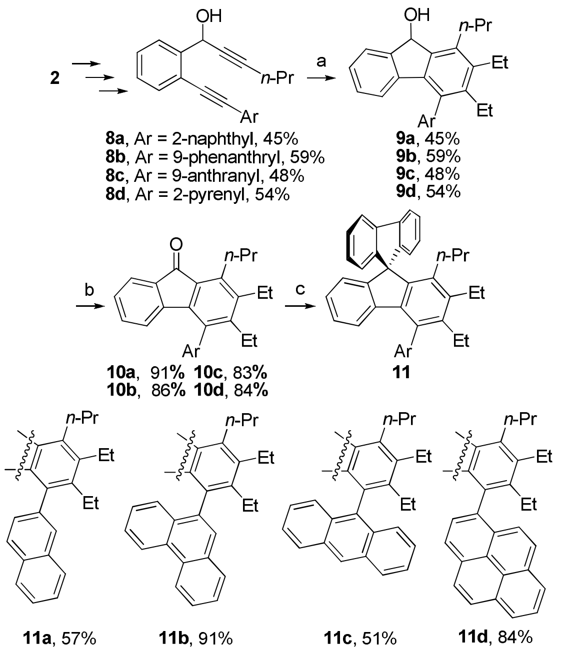

[a] $RhCl(PPh_3)_3$ (3 mol%), THF, Ag_2CO_3, 1.5 h, 180 °C
[b] DCC, CH_2Cl_2, 20 °C.
[c] 1: 2-LiC_6H_4-Ph, THF, -78 to 20 °C, 3h; 2: 12M HCl, AcOH .

Scheme 5. Synthesis of **11a-11d** with extended aromatic π-systems.

The set of four 9,9´-spirobifluorenes **11a-11d** with extended π-aromatic hydrocarbon systems was also investigated for their photophysical properties. All measured compounds exhibit different absorption spectra in the range of λ_{abs} = 250-330 nm (Table 3 and Figure 5). The emission quantum yields (Φ_s) of the derivatives exhibit low Φ_s = 0.11-0.12 except of **11c**, with Φ_s = 0.87. The emission bands show a high red shift into the visible blue region. For **11b**: λ_{em} = 353, 370, 391, 413 nm.The emission spectra for **11c** and **11d** had a similar structure of emission spectra to condensed aromatic hydrocarbons anthracene and pyrene but red shifted by ~30 and ~10 nm.[15] The sample **11a**, possessing the naphthyl group did not exhibit any emission at all.

Table 3. Photophysical properties for **11** (in cyclohexane).

Compound	λ_{abs}/nm ($\varepsilon/10^4 \cdot mol^{-1} \cdot dm^3 \cdot cm^{-1}$)	λ_{exc}/nm	λ_{em}/nm	Φ_s [a)]
11a	229 (1.2), 270 (sh), 282 (sh), 299 (sh), 312 (0.2)	-	-	-
11b	215 (sh), 228 (sh), 231 (sh), 249 (sh), 255 (sh), 270 (sh), 279 (sh), 289 (sh), 300 (sh), 312 (0.1)	267	353,370, 391, 413	0.12
11c	219 (sh), 220 (sh), 260 (1.1), 282 (sh), 299 (sh), 312 (0.1), 361 (sh), 380 (0.1), 401 (0.1)	270	405, 429,454	0.80
11d	237 (sh), 246 (1.0), 267 (sh) , 278 (0.7), 300 (0.2), 312 (0.3), 328 (0.3), 345 (0.5)	267	378, 389, 398	0.11

[a)] Quantum yields were calculated relative to DPA (Φ_r = 0.97).

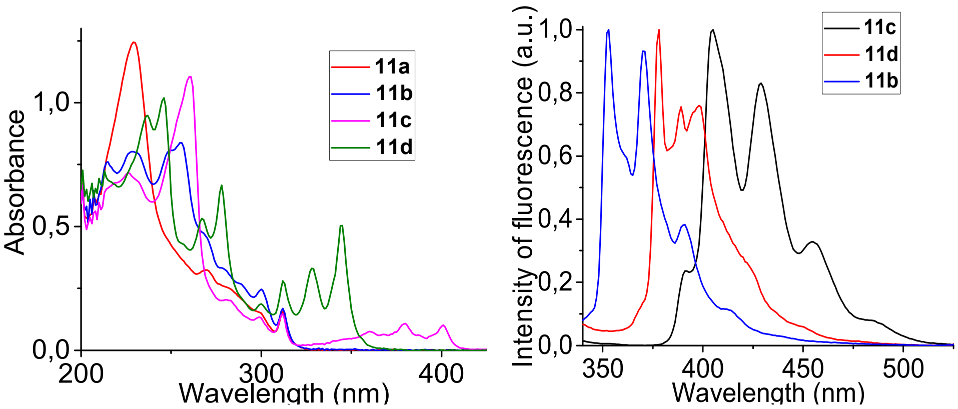

Figure 5. Absorption (left) and emission (right) spectra of **11a-11d**.

Finally, having the 9,9´-spirobifluorenes with the internal triple bonds **7** we decided to investigate also the influence of carborane structures with regard to absorption and emission properties. It was shown that suitably 1,2-aryl substituted carboranes and their related compounds may have interesting photophysical properties due to the a "Face-On" conformation of the aryl moieties with respect to each other. Hence we were curious whether a synthesis of fluorene derived carborane might have similar behavior.[16] **7a** was reacted with 6,9-$(Me_2S)_2$-*arachno*-$B_{10}H_{12}$ under standard conditions[17-19] to give

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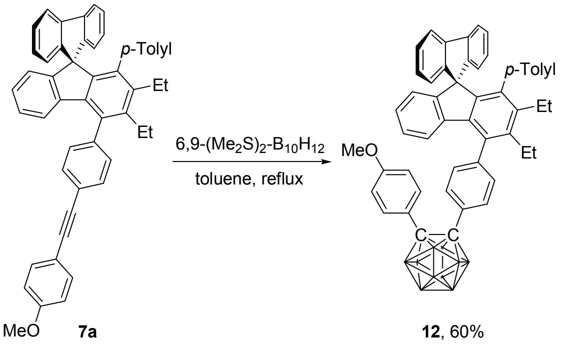
1,2-disubstituted carborane **12** (Scheme 6). The desired product was obtained in 60% isolated yield (and its structure was again unequivocally confirmed by a single crystal X-ray structure analysis (Figure 6).



Scheme 6. Reaction of $6,9\text{-}(Me_2S)_2$-*arachno*-$B_{10}H_{12}$ with alkyne **7a**.

The X-ray diffraction data revealed that whereas for **7a** the angle between the mean plane of the attached phenyl rings and the phenyl ring of the fluorene scaffold is only 74.8° and no considerable deformation or twisting between the phenyl units of the fluorene scaffold was observed being 6.8°. The photophysical properties of carborane containing molecule **12**was investigated as well. It exhibited similar absorption spectrum to spirobifluorenes**4** in the range of λ_{abs} = 250-330 nm, but revealed no emission.

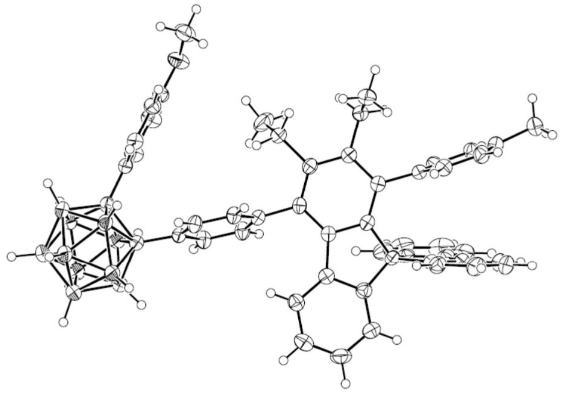


Figure 6.PLATON drawing of **12** showing displacement ellipsoids on the 50% probability level.

Conclusions

In summary, sets of 12 differently *4-substituted* 1-phenyl-2,3-diethyl-9,9´-spirobifluorenes have been synthesized and their photophysical properties have been examined. In addition, the synthesis nicely demonstrate extension of the previous method for regioselective synthesis of fluorenols based on rhodium-catalyzed cyclotrimerization reactions of diynes and alkynes with a high functional group tolerance. A study of photo-physical properties of the corresponding 9,9´-spirobifluorenes showed that the presence of various substituents (based on aromatic systems) in the position 4 affects the position of emission bands in the range of λ_{em} = 330-460 nm (in cyclohexane) and in many cases leads to high quantum yields of emission (Φ_s = 0.67-1.00). Namely, the presence of phenyl rings with electron accepting substituents in *para* position or other condensed aromatic systems induces the red shift of emission bands. It was demonstrated that the presence of trifluoromethylphenyl group causes a red shift of 28 nm in comparison with phenyl substituted derivative (**4d**), the shift is more than twice larger than the shift induced by pyridyl groups. From a general point of view, it should be taken in to account that emission spectra of the prepared derivatives are generally blue shifted in comparison with derivatives that do not bear substituents in the positions 2 and 3. The blue shift is probably caused by a large dihedral angle between the substituent in the position 4 and the fluorene scaffold leading to disruption of π-conjugation. Nonetheless, it is reasonable to presume that a similar effect, i.e. red shift of emission peaks induced by the presence of benzene ring possessing an electron withdrawing substituents in the position 4, could be observed also in simple 4-substituted 9,9´-spirobifluorenes. These results thus might provide useful information for further design of other substituted 9,9´-spirobifluorenes making them interesting potential materials for blue light emitting OLEDs and for further research.

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Conflict of interest

The authors declare no competing financial interest.

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