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Triptycene: No Homoconjugation Effect for Extending Optical Properties of π-Conjugated Oligomers

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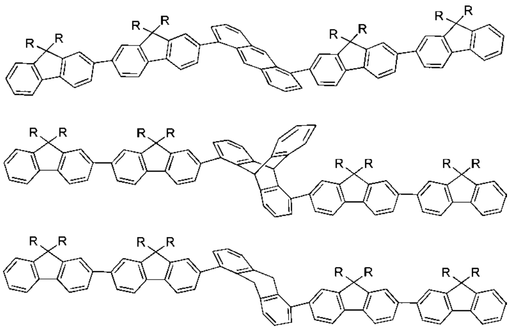
ABSTRACT



1,5- and 1,8-bis(bifluorenyl)anthracene were synthesized and converted to their corresponding bis(bifluorenyl)triptycenes and bis(bifluorenyl)-9,10-dihydroanthracenes. Analysis of their optical properties shows no feature of extended conjugation in the triptycene pair. The electronic spectra of the triptycene and dihydroanthracene pairs are in fact superimposable. There is definite evidence that triptycene displays zero homoconjugation effect.

Recent advances[1] in the studies of π-conjugated oligomers have continued to establish that they are well-suited photoluminescent materials for applications in organic optoelectronic/semiconductor devices and chemical sensors. Studies of a series of π-conjugated oligomers **1**[2] alternated by sp^3 centers suggested effective homoconjugation via the linker, and strong evidence of such extended homoconjugation was clearly illustrated in examples such as **2**[3] and **3**.[4] A similar observation was also made in their corresponding polymers.[2,4,5] Iptycenes (triptycene is the smallest member) have also been targets for constructing new molecules and materials.[6] The electronic spectrum of tripytcene **4**[7] or its derivatives showed inconclusive homoconjugation among the benzene rings. Charge-transfer,[8] circular dichroism,[9] and photoelectron spectroscopic studies[10] of derivatives of **4** however gave clear evidence of transannular interactions. Recently reported triptycene-based polymers such as **5**,[11] **6**,[12] and **7**[13] exhibit red-shifts from reference compounds in their

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(1) (a) Abbel, R.; Schenning, A. P. H. J.; Meijer, E. W. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 4215–4233. (b) Kanibolotsky, A. L.; Perepichka, I. F.; Skabara, P. J. *Chem. Soc. Rev.* **2010**, *39*, 2695–2728. (c) Kim, E.; Park, S. B. *Chem. Asian J.* **2009**, *4*, 1646–1658.

(2) (a) Martínez, A. G.; Barcina, J. O.; Fresno Cerezo, A.; Schlüter, A.-D.; Frahn, J. *Adv. Mater.* **1999**, *11*, 27–31. (b) Fáber, R.; Staško, A.; Nuyken, O. *Macromol. Chem. Phys.* **2000**, *201*, 2257–2266. (c) Rosso, P. G.; Almassio, M. F.; Antollini, S. S.; Garay, R. O. *Opt. Mater.* **2007**, *30*, 478–485.

(3) Caraballo-Martínez, N.; Rosario Colorado Heras, M.; Blázquez, M. M.; Barcina, J. O.; Martínez, A. G.; Rosario Torres Slvador, M. *Org. Lett.* **2007**, *9*, 2943–2946.

(4) Barcina, J. O.; Rosario Colorado Heras, M.; Mba, M.; Aspe, R. G.; Herrero-García, N. *J. Org. Chem.* **2009**, *74*, 7148–7156.

(5) Fáber, R.; Staško, A.; Nuyken, O. *Macromol. Chem. Phys.* **2001**, *202*, 2321–2327.

(6) Chong, J. H.; MacLachlan, M. J. *Chem. Soc. Rev.* **2009**, *38*, 3301–3315.

(7) (a) Theilacker, W.; Albrecht, K.; Uffmann, H. *Chem. Ber.* **1965**, *98*, 428–432. (b) Skvarchenko, V. R.; Shalaev, V. K.; KIabunovskii, E. I. *Russ. Chem. Rev.* **1974**, *43*, 951–966. (c) Brodskaya, E. I.; Ratovskii, G. V.; Voronkov, M. G. *Russ. Chem. Rev.* **1993**, *62*, 919–933.

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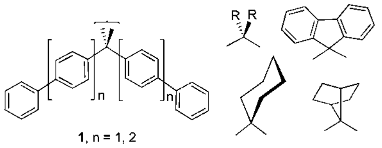
electronic spectra indicative of homoconjugation. The oligomer **8**[14] however indicates nonconjugation in the triptycene core.



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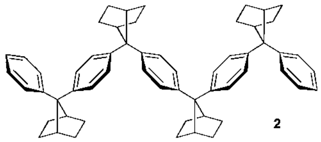

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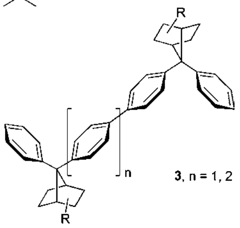

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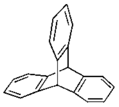

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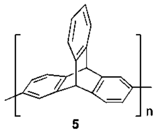

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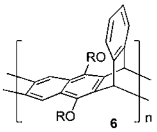

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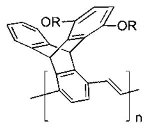

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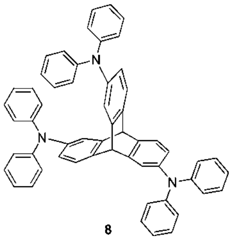

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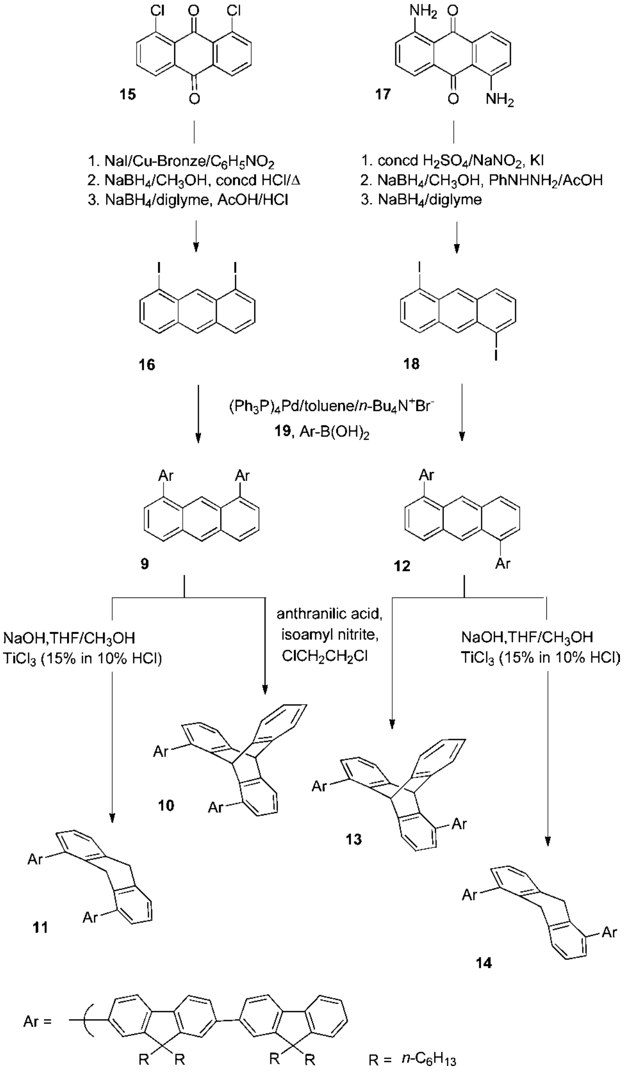
There was no direct and convincing comparative studies to substantiate the presence or lack of homoconjugation effect of a triptycene linker in sustaining optoelectronic properties of neutral π-conjugated oligomers. We report the synthesis and optical properties of the two series of oligomers, namely, **9**, **10**, and **11** and **12**, **13**, and **14** (Scheme 1). Our results have shown that there is zero homoconjugation effect via the triptycene linker in **10** and **13**.

Scheme 1. Synthesis of the Two Series of Oligomers: **9**, **10**, and **11** and **12**, **13**, and **14**



1,8-Diiodoanthracene **16** was prepared from dichloroanthraquinone **15** following a reported sequence[15] with minor modifications. 1,5-Diiodoanthracene **18** was however obtained from diaminoanthraquinone **17** in two steps following a separate report.[16] Suzuki coupling reactions between the boronic acid **19**[17] with diiodoanthracenes **16** and **18** gave the oligomers **9** and **12** in 59% and 54% yield, respectively. These were isolated as yellow oils. Diels−Alder reactions[18] between the benzyne generated from anthralinic acid and diarylanthracenes **9** and **12** afforded the triptycene-based oligomers **10** and **13**, respectively. These were isolated as colorless oils. Birch reduction[19] of **9** and **12** using aqueous $TiCl_3$ gave, respectively, the diaryldihydroanthracenes **11** and **14** as colorless oils. Two reference compounds, namely, **21** and **22**, were also prepared via Suzuki coupling reactions between boronic acid **20** and diiodoanthracenes **16** and **18**, respectively.

Transannular $\pi-\pi$ electronic interactions could be studied by electronic spectroscopy. Using the Clar's α, ρ, β, and β' notation,[20] the λ_{max} values of the principal bands of **9**−**14**

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(8) (a) Yamamura, K.; Nakasuji, K.; Murata, I.; Inagakic, S. *Chem. Commun.* **1982**, 396–397. (b) Murata, I. *Pure Appl. Chem.* **1983**, *55*, 323–330. (c) Harada, N.; Uda, H.; Nakasuji, K.; Murata, L. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1449–1453.

(9) Harada, N.; Tamai, Y.; Hisashi Uda, H. *J. Am. Chem. Soc.* **1980**, *102*, 506–511.

(10) (a) Ohno, K.; Ishida, T.; Naitoh, Y.; Izumi, Y. *J. Am. Chem. Soc.* **1985**, *107*, 8082–8086. (b) Martin, H.-D.; Mayer, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 283–314.

(11) Chen, Z.; Swager, T. M. *Macromolecules* **2008**, *41*, 6880–6885.

(12) (a) Thomas, S. W.; Long, T. M.; Pate, B. D.; Kline, S. R.; Swager, T. M. *J. Am. Chem. Soc.* **2005**, *127*, 17976–17977. (b) Chen, Z.; Amara, J. P.; Thomas, III, S. W.; Swager, T. M. *Macromolecules* **2006**, *39*, 3202–3209.

(13) Kim, Y.; Zhu, Z.; Swager, T. M. *J. Am. Chem. Soc.* **2004**, *126*, 452–453.

(14) Chou, H.-H.; Shih, H.-H.; Cheng, C.-H. *J. Mater. Chem.* **2010**, *20*, 798–805.

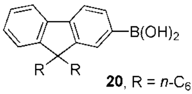
(15) Lovell, J. M.; Joule, J. A. *Synth. Commun.* **1997**, *27*, 1209–1215.

(16) Kendall, J. K.; Shechter, H. *J. Org. Chem.* **2001**, *66*, 6643–6649.

(17) Kanibolotsky, A. L.; Berridge, R.; Skabara, P. J.; Perepichka, I. F.; Bradley, D. D. C.; Koeberg, M. *J. Am. Chem. Soc.* **2004**, *126*, 13695–13702.

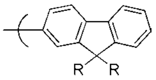
(18) Rybáčková, A.; Bělohradský, M.; Holý, P.; Pohl, R.; Dekoj, V.; Závada, J. *Synthesis* **2007**, *10*, 1554–1558.

(19) Jiang, J.; Lai, Y.-H. *Tetrahedron Lett.* **2003**, *44*, 1271–1274.



20, R = n-C_6H_{13}

Ar =



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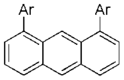

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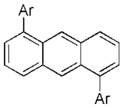

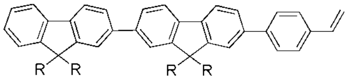

23, R = n-C_6H_{13}

are compared to those of reference compounds **21**, **22**, and **23**[21] (Figures 1−3; Table 1). Going from the pair of bis(fluorenyl)anthracenes **21** and **22** to the pair of bis(bifluorenyl)anthracenes **9** and **10**, respectively, there are significant bathochromic shifts in all absorption bands (Figure 1; Table 1). In particular, large changes are observed in λ_{max} of the ρ (>84 nm) and β (>57 nm) bands although the α bands in the spectra of **9** and **12** are not observable. The above is a clear indication of extended conjugation in **9** and **12** compared to **21** and **22**, respectively. The photoluminescence emission spectra (Figure 1; Table 1) of **9**, **12**, **21**, and **22** are however very similar. The optical bandgaps, estimated from the onset wavelength of the absorption spectrum, are essentially identical for **9**, **21**, and **24**, with that of **12** being marginally smaller (Table 1).

Significant changes are clearly observed in their absorption spectra going from the pair of **9** and **12** to those of **10** and **13**, respectively, after replacing anthracene with a triptycene linker (Figure 2). Although their λ_{max} values (Table 1) are very similar to those of **9** and **10**, the β absorption bands of **12** and **13** decline drastically to baseline (Figure 2). No appreciable ρ band is observable in either spectrum. This is essentially a conclusive indication that there is no appreciate homoconjugation effect through the triptycene linker in **10** and **13**. Their estimated optical bandgaps (Table 1) are thus as expected significantly larger than those of **9** and **12**. Their emission λ_{max} values are also considerably shifted from those observed for **9** and **12**. On the other hand, the absorption and emission properties of **10** and **13** closely resemble those of a "monomeric" reference compound **23**[21] (Table 1). This further suggests that the two side arms in **10** or **13** behave like isolated phenyldifluorenyl entities.

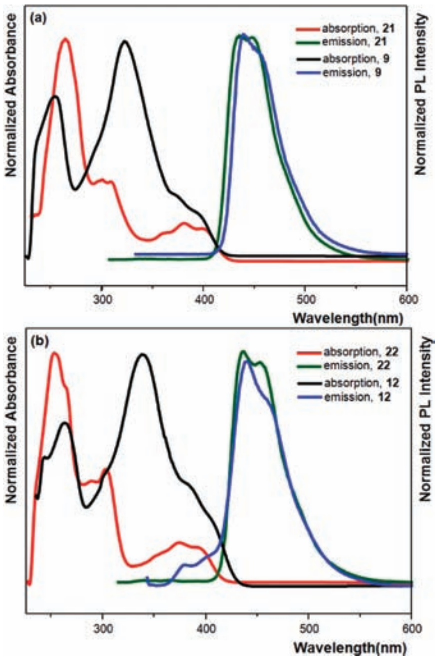

Figure 1. Normalized absorption and emission spectra of (a) **9** and **21** and (b) **12** and **22** in chloroform.

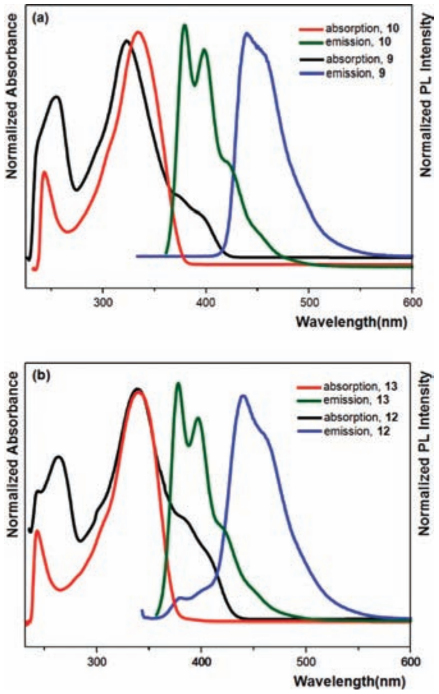

Figure 2. Normalized absorption and emission spectra of (a) **9** and **10** and (b) **12** and **13** in chloroform.

The central ring in 9,10-dihydroanthracene was shown to assume a boat conformation[22] with a folding angle of ca. 141° by theoretical computations[23] and 145° in X-ray crystallographic studies.[24] The dihydroanthracene linker in **11** and **14** is expectecd to adopt a similar boat conformation. With a large folding angle, there should be no favorable transannular $\pi-\pi$ interactions between the conjugated units at the two sides. As shown in Figure 3, the absorption and emission spectra of **11** and **14** are essentially superimpossible with those of **10** and **13**,

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[20] Clar, E. *Polycyclic Hydrocarbons*; Academic Press-Springer-Verlag: London, 1964; Vol. 2, p 116.

[21] Sugiyama, K.; Hirao, A.; Hsu, J.-C.; Tung, Y.-C.; Chen, W.-C. *Macromolecules* **2009**, *42*, 4053–4062.

[22] (a) Sánchez, M.; Parella, T.; Cervelló, E.; Jaime, C.; Virgili, A. *Magn. Reson. Chem.* **2000**, *38*, 925–931. (b) Shishkin, O. V. *Russ. Chem. Bull.* **1997**, *46*, 1981–1991. (c) Rabideau, P. W. *Acc. Chem. Res.* **1978**, *11*, 141–147.

[23] Schaefer, T.; Sebastian, R. *J. Mol. Struct. (Theochem)* **1987**, *153*, 55–58.

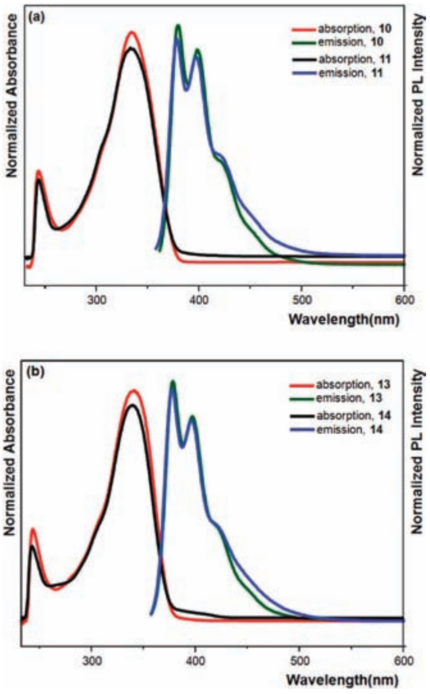

Figure 3. Normalized absorption and emission spectra of (a) **10** and **11** and (b) **13** and **14** in chloroform.

respectively. This is another piece of strong evidence that triptycene offers zero homoconjugation effect in **10** or **13**.

In conclusion, we have successfully synthesized two series of oligomers, namely, **9**→**10**→**11** and **12**→**13**→**14**, going from a central anthracene to a triptycene to a dihydroanthracene spacer. Systematic studies of their optical properties have provided definite evidence that triptycene offers zero homoconjugation effect. This is contrary to observed homoconjugation in derivatives[8−10] of triptycene that incorporate larger benzenoid systems or highly polar substituents to the triptycene skeleton to facilitate transannular charge-transfer interactions. That electronic interaction, if any, between the remote benzene rings in the parent triptycene is ineffective in propagating extended π-conjugation in observable optical properties is no longer a controversy. Our results should discourage any future attempt in the study of π-conjugated oligomers as functional materials employing neutral triptycene as a homoconjugation linker.

Table 1. Comparison of Optical Properties of Compounds **9**−**14** and **21**−**23**

	absorbance λ_{max}[a]					
compd	α	ρ	β	β'	PL λ_{max}	E_g[c] (eV)
9	—	(392)[b]	322	254	440, (455)[b]	2.96
10	—	—	334	243	379, 398	3.26
11	—	—	333	243	378, 397	3.28
12	—	(406)[b]	338	263	439, (462)[b]	2.87
13	—	—	341	243	378, 397	3.28
14	—	—	340	243	378, 397	3.32
21	400	308	265	—	434, 466	2.94
22	392	303	253	—	435, 453	2.96
23[21]	—	—	346	—	388, 409	—

[a] λ_{max} at the longest wavelength of each absorption band is shown. [b] Shoulder peak. [c] Bandgap estimated from the onset wavelength of the absorption spectrum.

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Supporting Information Available: Experimental and spectroscopic data of compounds **9**−**14** and **21**−**22**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) (a) Ferrier, W. G. W. G.; Iball, J. J. *Chem. Ind. (London)* **1954**, 1296–1297. (b) Herbstein, F. H.; Kapon, M.; Reisner, G. M. *Acta Crystallogr*. **1986**, *B42*, 181–187.