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Helicene Monomers and Dimers: Chiral Chromophores with Outstanding Circularly Polarized Luminescence

Dedicated to Professor Dr. Martin Quack

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Abstract: We report the synthesis and chiroptical properties of a series of enantiomerically pure, C_2-symmetrical carbo[6]helicene dimers. Two helicene cores are connected through a buta-1,3-diyne-1,4-diyl linker or a heteroaromatic bridge and bear arylethynyl substituents at their 15-positions. This ensures the possibility of extended electronic communication throughout the whole molecule. The new chromophores exhibit intense ECD spectra with strong bands in the UV/Vis region well above 400 nm. The anisotropy factor g_{abs} (defined as $\Delta\varepsilon/\varepsilon$) reaches values up to 0.047, which are unusually large for single organic molecules. They also display blue fluorescence, with good quantum yields ($\Phi_f \sim 0.25$). The emitted light is circularly polarized to an outstanding extent: in some cases, the luminescence dissymmetry factor $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$ attains values of $|0.025|$. To the best of our knowledge, such values are among the highest ever reported for non-aggregated organic fluorophores.

Fluorescence is a privileged physical property, and fluorescent materials find a wide range of applications, such as in medical diagnostics, chemical sensors, and optoelectronic devices (e.g. in circularly polarized OLEDs).[1] Circular polarized luminescence (CPL) has gained increasing interest for its possible application in optical information storage and transfer, where the extent of CPL can add a further dimension to the information content conveyed by light.[1] Highly CPL-active compounds were found mostly among chiral lanthanide complexes, but the interest of material scientists in chiral, molecular organic emitters also heightened more recently.[2]

Helicenes are an extensively investigated class of chiral organic compounds, presenting strong UV/Vis and electronic circular dichroism (ECD) intensities,[3] but usually displaying low fluorescence quantum yields (Φ_f).[4] Recently, polycyclic aromatic hydrocarbons,[5] with helicenes amongst them,[6] have been developed with higher fluorescence quantum yields and CPL activity, leading to their investigation for novel applications such as in spintronics.[7] Fluorescent helicene design has relied mostly on the introduction of heterocycles[8] into the helicene backbone, such as thiophene,[9] pyrrole,[10] or furan[11] rings. So far, the discovery of efficient, all-carbon helicene fluorophores has not widely been reported.

The interest in the design of enantiopure fluorescent helicenes relies also on their ability to emit left- and right-circularly polarized light with different intensities (CPL). Usually, CPL is quantified through the luminescence dissymmetry factor g_{lum}, which is defined as the ratio between the difference of the left and right circularly polarized light and the half of the total luminescence. By definition, $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, ($I$ = intensity of circularly polarized light) can range from -2 (when the emitted light is totally right-circularly polarized) to $+2$ (the emitted light is totally left-circularly polarized). In most cases, the g_{lum} factors of helicenic fluorophores are in the 10^{-3}–10^{-4} range, similarly to those of other non-aggregate organic molecules.[2b, 6, 12]

Recently, we reported a novel class of enantiomerically pure, buta-1,3-diyne-1,4-diyl linked carbo[6]helicene oligomers.[13] Dimeric $(+)$-$(P)_2$- and $(-)$-$(M)_2$-**1** displayed moderate fluorescence quantum yields ($\Phi_f = 0.11$). Starting from dimeric $(P)_2$-**1**, we obtained by heteroaromatization[14] thiene-2,5-diyl linked $(+)$-$(P)_2$-**2**,[13] which displayed an increased Φ_f value of 0.25, one of the highest Φ_f values reported to date for a carbohelicene. We proposed that the fluorescence of $(P)_2$-**2** originated from the push-pull substitution on the helicene cores, with the thienyl ring as electron donor and the alkynes as acceptors and thus set out to further validate this hypothesis.

Here, we explore the push-pull effects by changing the thienyl to a pyrrole ring (Figure 1), resulting in *N*-phenylpyrrole-2,5-diyl linked compound $(+)$-$(P)_2$- and $(-)$-$(M)_2$-**3**. We also substituted the ethynyl residues at the C-15 position of thiene-2,5-diyl linked $(P)_2$- and $(M)_2$-**2** (Figure 1). The different substituents include electron-withdrawing 4-nitrophenyl in $(+)$-$(P)_2$- and $(-)$-$(M)_2$-**4** and 4-cyanophenyl in $(+)$-$(P)_2$- and $(-)$-$(M)_2$-**5**, fluorophoric pyren-1-yl in $(+)$-$(P)_2$- and $(-)$-$(M)_2$-**6**, and electron-donating *N,N*-dimethylanilino in $(+)$-$(P)_2$- and $(-)$-$(M)_2$-**7** (Figure 1). The optical and chiroptical properties of $(P)_2$- and $(M)_2$-**1**–**7** and monomeric (P)- and (M)-**8** and **9** were studied by UV/Vis, ECD, fluorescence, and CPL spectroscopy. The investigation revealed very strong optical absorption properties (UV/Vis $\varepsilon \sim 10^5$ M^{-1} cm^{-1} and ECD $\Delta\varepsilon \sim 400$ M^{-1} cm^{-1}), and uncharacteristically large fluorescence ($\Phi_f = 0.25 - 0.35$) and CPL activities (g_{lum} up to $|0.025|$), of substantial interest for applications as chiral fluorescent materials.

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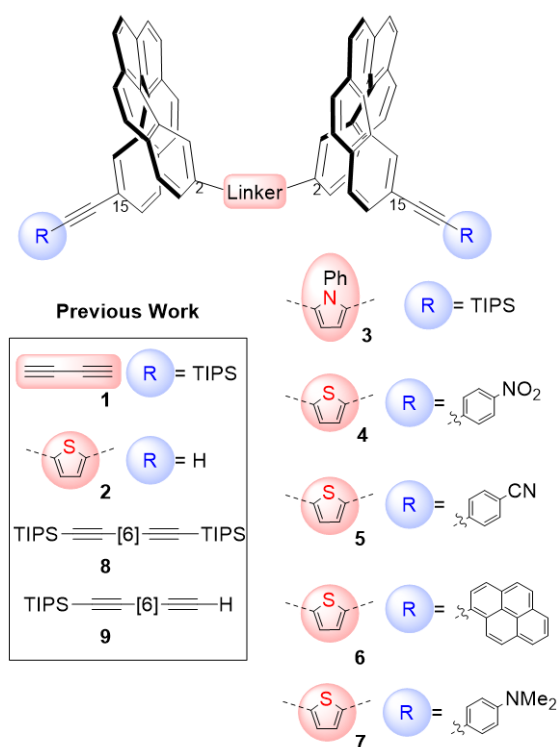
Figure 1. Schematic representation of fluorescent [6]helicenes (*P*)₂-**1**–**7**. Compounds (*P*)₂-**2** and (*P*)₂-**4**–**7** are linked by thiene-2,5-diyl and capped by different end groups of varying chromophoric and electronic properties (blue). Dimer (*P*)₂-**3** is linked by pyrrole-2,5-diyl and capped with triisopropylsilyl (TIPS) groups. Dimers (*P*)₂-**1** and (*P*)₂-**2**, and monomers (*P*)-**8** and (*P*)-**9** (shown only in abbreviated form with –[6]– being the carbo[6]helicene with the substitution pattern shown in the dimers; for full structures, see the Supporting Information) were reported in our earlier communication.[13]

The synthesis of (*P*)₂-**3** proceeded in 35% by the copper(I) catalyzed heteroaromatization reaction with aniline.[14] The corresponding furan-2,5-diyl linked dimeric helicene could not be obtained by the reported protocol.[14] The other target compounds were prepared by Pd-catalyzed Sonogashira cross-coupling[15] of (*P*)₂-**2** with various aryl iodides, which provided (*P*)₂-**4**–**7** in yields ranging between 19% and 61%. Aryl bromides proved to be unreactive under various conditions. Synthesis and full characterization of all new compounds are reported in Sections S2 and S3 in the Supporting Information.
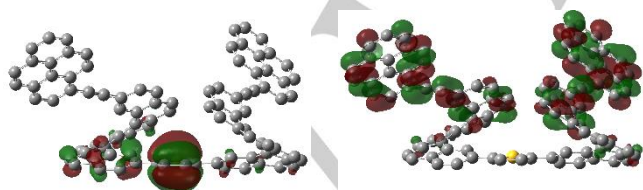
Figure 2. Calculated (DFT/B3LYP/cc-pVDZ using Gaussian 09 Rev. D01) frontier molecular orbitals of (*M*)₂-**6**. (left) The HOMO is mostly localized on the thiene-2,5-diyl linker and the proximal benzene rings, while the (right) LUMO shows the electron delocalization on the pyrenylacetylenes at the C-15 positions, suggesting the desired push-pull effect is achieved.

Density functional theory (DFT) calculations were performed using Gaussian 09 Rev. D01 to assign absolute configurations and forecast the expected push-pull effects of the prospective compounds.[16]

Each compound was optimized by DFT calculations at the B3LYP/cc-pVDZ level of theory (see Section S6 in the Supporting Information). We compared the electronic density delocalization of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of dimers (*M*)₂-**1** and (*M*)₂-**6**. While (*M*)₂-**1** showed full delocalization of the electronic density map of the HOMO and LUMO over the entire dimer,[13] these orbitals in (*M*)₂-**6** revealed a remarkable change. While the electron density of the HOMO is concentrated around the central thiophene core and the proximal benzene rings (Figure 2a), the LUMO features the highest density on the outer helicene benzene rings (Figure 2b), with delocalization extending into the pyrenylethynyl moieties. This image is reminiscent of intra-molecular push-pull chromophores.[17]

The electronic and geometric preferences of thiene-2,5-diyl linked (*M*)₂-**2** and pyrrole-2,5-diyl linked (*M*)₂-**3** are difficult to compare due to the steric influence of the bulky phenyl substituent on the pyrrole ring in the latter. The spectral and conformational properties of (*M*)₂-**3** are discussed and compared to (*M*)₂-**2** in Sections S4 and S5 in the Supporting Information.

The UV/Vis and ECD spectra of enantiomerically pure (*P*)₂- and (*M*)₂-**2**–**7** are shown in Figure 3 and in Section S4 of the Supporting Information, and the major absorption bands are reported in Table 1. We had previously noted a red-shift in the highest-wavelength absorbance of thiene-2,5-diyl linked (*P*)₂-**2** relative to buta-1,3-diyne-1,4-diyl linked (*P*)₂-**1**,[13] but this was not observed for the pyrrole-2,5-diyl linked (*P*)₂-**3** (Figure 3 top). Similarly, the UV/Vis spectra of the doubly arylalkynylated compounds, such as (*P*)₂-**7** (Figure 3 bottom), revealed only minor changes, differing only in spectral shapes (see also Figures S1 and S2 in the Supporting Information) from (*P*)₂-**2**, but showing similar maximal absorbance at ~450 nm. In general, the dimeric carbo[6]helicenes all feature very strong UV/Vis absorptions and ECD bands, non-linearly enhanced with respect to the corresponding monomers (*P*)-**8** or (*P*)-**9**, a remarkable feat that is still difficult to achieve for helicenes reported to date.[13,18]

The ECD spectra of dimeric (*P*)₂-**2**–**7** (Figure 3 and Figures S3 and S4 in the Supporting Information) revealed a blue-shift in the first Cotton effect of pyrrole-2,5-diyl linked (*P*)₂-**3** compared to the thiene-2,5-diyl linked compounds (*P*)₂-**2** and (*P*)₂-**4**–**7**. For all new dimers, the overall intensity of the higher-energy ECD bands was reduced compared to (*P*)₂-**1**. Interestingly however, bis-pyrenyl derivative (*P*)₂-**6** showed three strong bands in the ECD spectrum at 308, 412, and 430 nm with $\Delta\varepsilon$ values 200–400 [M⁻¹ cm⁻¹]. These Cotton effects are much less pronounced in the other spectra (Figure 3 and Figure S4 in the Supporting Information). These strong ECD bands reflect the pyrene absorption bands, but the chirality induction from the helicene into the achiral pyrene moieties is quite remarkable.
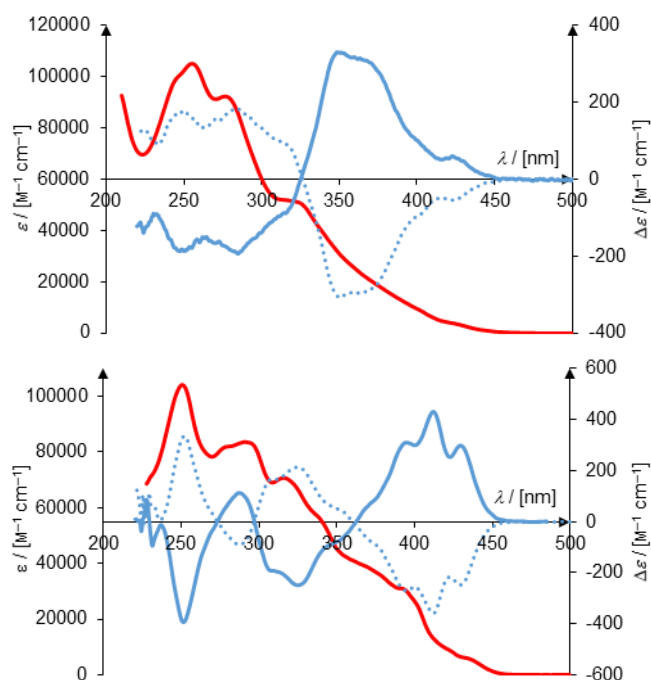
Figure 3. UV/Vis (red line) and ECD spectra (blue line) of $(P)_2$-**3** (top) and $(P)_2$-**6** (bottom). Dotted lines represent the $(M)_2$-enantiomers. UV/Vis and ECD experiments were performed in CH_2Cl_2 at 23 °C ($c \sim 10^{-6}$ M and $c \sim 10^{-7}$ M, respectively). See Section S4 in the Supporting Information for further spectra of $(P)_2$- and $(M)_2$-**2**–**7**.

Table 1. Optical and chiroptical properties of the new dimers $(P)_2$-**3**–**7** in comparison to the data for the previously published dimers $(P)_2$-**1** and **2** and monomers (P)-**8** and **9**. Shown are the intensities (ε) of the ^1B_b and ^1B_a absorption bands,[19] the absorption anisotropy factors g_{abs} ($= \Delta\varepsilon/\varepsilon$) at ≈ 430 nm, the fluorescence emission bands (λ_{em}), the absolute fluorescence quantum yields measured by integrating sphere (Φ_f),[20] and the CPL factor $|g_{lum}| = 2\,\Delta I\,/\,I$ (I = intensity of circularly polarized light).

	ε [1000 M^{-1} cm^{-1}]		$|g_{abs}|$	λ_{em} [nm]	Φ_f	$|g_{lum}|$
	^1B_b [a]	^1B_a [b]				
$(P)_2$-**1**[13]	108	120	0.02	424, 449	0.11	0.02
$(P)_2$-**2**[13]	57	103	0.01	454, 481	0.25	0.012
$(P)_2$-**3**	61	105	0.01	507	0.27	0.008
$(P)_2$-**4**	52	54	0.01	n.d.	<0.01	n.d
$(P)_2$-**5**	82	81	0.01	456, 483	0.28	0.01
$(P)_2$-**6**	70	104	0.047[c]	458, 484	0.35	n.d
$(P)_2$-**7**	95	87	0.01	455, 480	0.28	0.012
(P)-**8**[13]	72	86	0.02	424, 449	0.05	0.025
(P)-**9**[13]	69	78	0.02	430, 454	0.05	0.018

[a] The ^1B_b[19] band can be seen at $\lambda = 310$–330 nm; [b] The ^1B_a[19] band can be seen at $\lambda = 250$–255 nm; [c] Cotton effects corresponding to higher-wavelength pyrene absorptions at $\lambda = 245$, 259, and 275 nm respectively, are probably at the origin of the large g_{abs} value. n.d. = not determined.

The absorption anisotropy factors g_{abs} (defined as $\Delta\varepsilon/\varepsilon$) range between 0.01–0.02 at $\lambda \approx 430$ nm for all dimeric compounds, with the exception of $(P)_2$-**6** (Figure 4).[13, 18a, 21] Indeed, helicenes are widely reported to generally display substantially larger anisotropy values than other chiral organic molecules. $(P)_2$-**6** stands out with a g_{abs} of 0.047 at $\lambda = 430$ nm and a second strong band with a g_{abs} of 0.034 at $\lambda = 414$ nm, values substantially higher than previously found.

The fluorescence spectra show that all thiene-2,5-diyl linked compounds $(P)_2$-**5**–**7** display a similar, structured emission pattern with a first emission band at $\lambda_{em} = 450$–460 nm and a second band at 480–485 nm, while $(P)_2$-**4** showed no noticeable emission (Figure S6 in the Supporting Information). This lack of emission is likely due to the fluorescence quenching properties of the nitro groups.[22] Similarly, no noticeable change in fluorescence quantum yield is observed ($\Phi_f = 0.25$–0.28) for $(P)_2$-**5** and $(P)_2$-**7** compared to parent $(P)_2$-**2**, while pyren-1-yl substituted $(P)_2$-**6** shows a substantially larger Φ_f value of 0.35 (Table 1) due to the inherent fluorescence of the pyrene moieties. The heteroaromatization of $(P)_2$-**1** ($\lambda_{em} = 424$ and 449 nm[13]) to $(P)_2$-**2** led to a red-shift in emission wavelength by 30 nm ($\lambda_{em} = 454$ and 481 nm) (Figure 5).[13] Replacing the thiene-linker by a pyrrole-linker to give $(P)_2$-**3** again afforded a second bathochromic shift of further 37 nm ($\lambda_{em} = 507$ nm, Table 1, the emission is no longer structured), revealing a strong impact of the linker moiety on the emission properties of the dimeric helicenes.
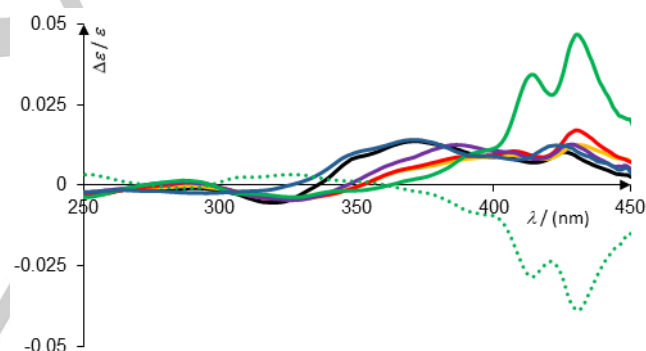

Figure 4. g_{abs}-Factor plot ($\Delta\varepsilon/\varepsilon$) in CH_2Cl_2 of $(P)_2$-**2** (black line),[13] $(P)_2$-**3** (blue line), $(P)_2$-**4** (purple line), $(P)_2$-**5** (yellow line), $(P)_2$-**6** (green line, $(M)_2$-enantiomer represented by the dotted green line), and $(P)_2$-**7** (red line). Only the $(M)_2$-enantiomer of **6** is shown in order to keep the Figure readable. Above 430 nm, the spectra contained artefacts since UV/Vis spectral intensities become vanishingly small. All spectra were recorded at 23°C at $c = 10^{-6}$ M.

The CPL properties of the enantiomers of **1**–**3**, **5**, and **7**–**9** in 0.3–0.6 mM CH_2Cl_2 solutions reveal very high g_{lum}-factors (Table 1). The g_{lum} values in all CPL spectra are very large, reaching $|0.025|$ for monomeric (P)- and (M)-**8** (black in Figure 5), which is higher than previously reported values for helicenes and for pure organic molecules in general.[10, 12, 23, 24] The dimeric carbohelicenes $(P)_2$- and $(M)_2$-**1 and monomeric** (P)- and (M)-**9** (Figure S7 in the Supporting Information)[13] also reach values of $|0.02|$. Thiene-2,5-diyl linked dimeric helicenes $(P)_2$- and $(M)_2$-**2** (dark blue in Figure 5) or pyrrole-2,5-diyl linked $(P)_2$- and $(M)_2$-**3** (green in Figure 5) displayed values in the range of $g_{lum} \sim |0.01|$. The substituents at the C-15 position in $(P)_2$-**5** and $(P)_2$-**7** (Figure S8) seem to have little impact on the CPL activity of the

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compounds, in line with our observations for the luminescence study above.

It is apparent that higher g_{lum} values are found for compounds $(P)_2$-**1**, (P)-**8**, and (P)-**9** containing no heteroatoms (except the silyl protecting groups) despite their lower fluorescence quantum yields Φ_f. A higher absolute fluorescence quantum yield does not necessarily lead to stronger CPL activity.[25] We currently do not have a full explanation for this observed superiority of our all-carbon systems over the heteroatom-substituted ones. We note however, that the magnitude of CPL could possibly be influenced by the number of acetylene moieties per molar mass in a molecule which appears to coincide with other CPL data reported for polycyclic aromatic hydrocarbons bearing multiple acetylene units.[24] Future research will hopefully help confirming why the all-carbon-backbone chromophores, dimeric $(P)_2$-**1** and monomeric (P)-**8** and (P)-**9**, display CPL intensities of such large magnitude as observed in our measurements (Figure 5 and Figure S7 in the Supporting Information).
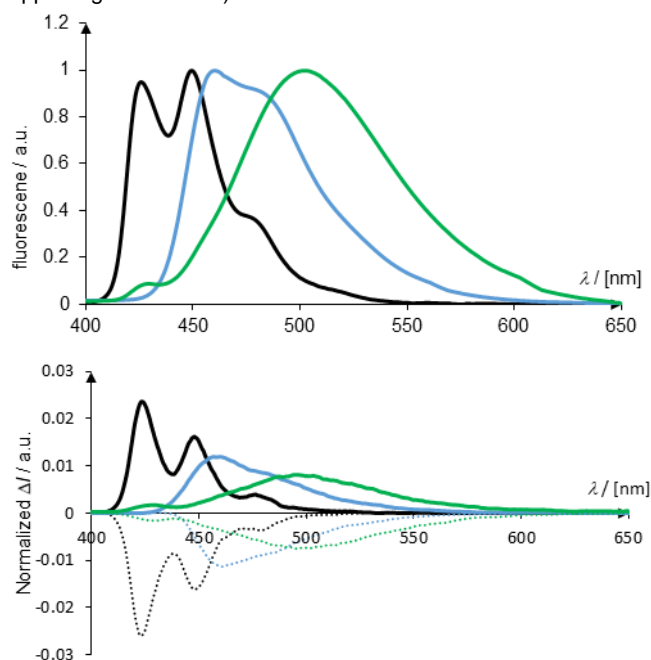
Figure 5. (top) Fluorescence and (bottom) CPL measurements of all-carbon monomeric helicene (P)-**8** (black), dimeric thiene-2,5-diyl linked $(P)_2$-**2** (light blue), and pyrrole-2,5-diyl linked $(P)_2$-**3** (green). Dotted lines correspond to the (M)-enantiomers. All experiments were performed in CH_2Cl_2 ($c \sim 0.3$–0.6 mM) at 23 °C. All CPL spectra of $(P)_2$- and $(M)_2$-**1**–**9** are shown in Figures S7 and S8 in the Supporting Information.

In conclusion, we report the synthesis of enantiopure bis[6]helicenes $(P)_2$- and $(M)_2$-**3**–**7** and subjected them, together with previously reported[13] dimeric $(P)_2$-**1** and **2** and monomeric (P)- and (M)-**8** and **9** to a comprehensive investigation by optical spectroscopy. The electronic absorption spectra feature bands with large molar extinction coefficients ($\varepsilon \sim$100'000 M^{-1} cm^{-1}) for the dimeric derivatives. The ECD responses also are intense and of particular interest in the case of bis(pyrene-1-yl) substituted $(P)_2$- and $(M)_2$-**6**, which showed high chiral induction from the enantiopure helicenes into the flat pyrene moieties, reflected in

large g_{abs}-factors of up to 4.7×10^{-2} for the pyrene-based longest wavelength absorptions. The new dimeric systems feature interesting luminescence properties with absolute fluorescence quantum yields (Φ_f) between 0.27 and 0.35. The emission wavelengths are strongly dependent on the linker between the two helicene cores. As the most prominent finding, all compounds displayed high CPL intensities, leading to large g_{lum} values in the $\sim 10^{-2}$ range and reaching values up to |0.025|. Remarkably, the g_{lum} values are highest for the pure carbon scaffolds, dimeric $(P)_2$-**1** and monomeric (P)-**8** and (P)-**9**, compared to the structurally comparable derivatives containing heteroatoms, which display higher fluorescence quantum yields. The reasons for this unexpected observation remain unclear, however at present we believe that they are related to the higher number of acetylene residues in the π-conjugated chromophores. These findings need further corroboration in future studies toward targeting applications, including spintronics.[7]

References

[1] a) E. Peeters, M. P. T. Christiaans, R. A. J. Janssen, H. F. M. Schoo, H. P. J. M. Dekkers, E. W. Meijer, *J. Am. Chem. Soc.* **1997**, *119*, 9909–9910; b) A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem. Int. Ed.* **1998**, *37*, 402–428; *Angew. Chem.* **1998**, *110*, 416–443; c) M. Oda, H. G. Nothofer, G. Lieser, U. Scherf, S. C. J. Meskers, D. Neher, *Adv. Mater.* **2000**, *12*, 362–365; d) Y. Geng, A. Trajkovska, S. W. Culligan, J. J. Ou, H. M. P. Chen, D. Katsis, S. H. Chen, *J. Am. Chem. Soc.* **2003**, *125*, 14032–14038; e) H. Kobayashi, M. Ogawa, R. Alford, P. L. Choyke, Y. Urano, *Chem. Rev.* **2010**, *110*, 2620–2640; f) B. Valeur, M. N. Berberan-Santos, *J. Chem. Educ.* **2011**, *88*, 731–738; g) Y. Yang, R. C. da Costa, D.-M. Smilgies, A. J. Campbell, M. J. Fuchter, *Adv. Mater,* **2013**, *25*, 2624–2628; h) F. Zinna, U. Giovanella, L. D. Bari, *Adv. Mater.* **2015**, *27*, 1791–1795; i) J. R. Brandt, X. Wang, Y. Yang, A. J. Campbell, M. J. Fuchter, *J. Am. Chem. Soc.* **2016**, *138*, 9743–9746; j) W.-G. Lu, X.-G. Wu, S. Huang, L. Wang, Q. Zhou, B. Zou, H. Zhong, Y. Wang, *Adv. Org. Mater.* **2017**, *5*, 1700594.

[2] a) J. P. Riehl, F. S. Richardson, *Chem. Rev.* **1986**, *86*, 1–16; b) E. M. Sánchez-Carnerero, A. R. Agarrabeitia, F. Moreno, B. L. Maroto, G. Muller, M. J. Ortiz, S. de la Moya, *Chem. Eur. J.* **2015**, *21*, 13488–13500; c) F. Zinna, L. Di Bari, *Chirality* **2015**, *27*, 1–13; d) G. Longhi, E. Castiglioni, J. Koshoubu, G. Mazzeo, S. Abbate, *Chirality* **2016**, *28*, 696–707.

[3] a) R. H. Martin, *Angew. Chem. Int. Ed.* **1974**, *13*, 649–660; *Angew. Chem.* **1974**, *86*, 727–738 b) A. Urbano, *Angew. Chem. Int. Ed.* **2003**, *42*, 3986–3989; *Angew. Chem.* **2003**, *34*, 4116–4119; c) P. Sehnal, I. G. Stará, D. Šaman, M. Tichý, J. Míšek, J. Cvačka, L. Rulíšek, J. Chocholoušová, J. Vacek, G. Goryl, M. Szymonski, I. Císařová, I. Starý, *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 13169–13174; d) M. Gingras, *Chem. Soc. Rev.* **2013**, *42*, 968–1006; e) M. Gingras, *Chem. Soc. Rev.* **2013**, *42*, 1051–1095; f) K. Mori, T. Murase, M. Fujita, *Angew. Chem. Int. Ed.* **2015**, *54*, 6847–6851; *Angew. Chem.* **2015**, *23*, 6951–6955; g) X.-Y. Wang, X.-C. Wang, A. Narita, M. Wagner, X.-Y. Cao, X. Feng, K. Müllen, *J. Am. Chem. Soc.* **2016**, *138*, 12783–12786; h) C.-F. Chen. Y. Shen, *Helicene Chemistry. From Synthesis to Applications*, Springer, Berlin, **2017**.

[4] a) J. B. Birks, D. J. S. Birch, E. Cordemans, E. Vander Donckt, *Chem. Phys. Lett.* **1976**, *43*, 33–36; b) M. T. Reetz, S. Sostmann, *Tetrahedron* **2001**, *57*, 2515–2520.

[5] a) H. Maeda, Y. Bando, K. Shimomura, I. Yamada, M. Naito, K. Nobusawa, H. Tsumatori, T. Kawai, *J. Am. Chem. Soc.* **2011**, *133*, 9266–9269; b) R. B. Alnoman, S. Rihn, D. C. O'Connor, F. A. Black, B. Costello, P. G. Waddell, W. Clegg, R. D. Peacock, W. Herrebout, J. G. Knight, M. J. Hall, *Chem. Eur. J.* **2016**, *22*, 93–96.

[6] a) N. Saleh, B. Moore, II, M. Srebro, N. Vanthuyne, L. Toupet, J. A. G. Williams, C. Roussel, K. K. Deol, G. Muller, J. Autschbach, J. Crassous, *Chem. Eur. J.* **2015**, *21*, 1673–1681; b) H. Isla, M. Srebro-Hooper, M. Jean, N. Vanthuyne, T. Roisnel, J. L. Lunkley, G. Muller, J. A. G. Williams, J. Autschbach, J. Crassous, *Chem. Commun.* **2016**, *52*, 5932–5935.

[7] V. Kiran, S. P. Mathew, S. R. Cohen, I. H. Delgado, J. Lacour, R. Naaman, *Adv. Mater.* **2016**, *28*, 1957–1962.

[8] A. Rajapakse, K. S. Gates, *J. Org. Chem.* **2012**, *77*, 3531–3537.

[9] Y. Yamamoto, H. Sakai, J. Yuasa, Y. Araki, T. Wada, T. Sakanoue, T. Takenobu, T. Kawai, T. Hasobe, *Chem. Eur. J.* **2016**, *22*, 4263–4273.

[10] T. Otani, A. Tsuyuki, T. Iwachi, S. Someya, K. Tateno, H. Kawai, T. Saito, K. S. Kanyiva, T. Shibata, *Angew. Chem. Int. Ed.* **2017**, *56*, 3906–3910; *Angew. Chem.* **2017**, *129*, 3964–3968.

[11] M. S. Sundar, A. V. Bedekar, *Org. Lett.* **2015**, *17*, 5808–5811.

[12] N. Saleh, M. Srebro, T. Reynaldo, N. Vanthuyne, L. Toupet, V. Y. Chang, G. Muller, J. A. G. Williams, C. Roussel, J. Autschbach, J. Crassous, *Chem. Commun.* **2015**, *51*, 3754–3757.

[13] C. Schaack, E. Sidler, N. Trapp, F. Diederich, *Chem. Eur. J.* **2017**, *23*, 14153–14157.

[14] Q. Zheng, R. Hua, *Tetrahedron Lett.* **2010**, *51*, 4512–4514.

[15] K. Sonogashira, *J. Organomet. Chem.* **2002**, *653*, 46–49.

[16] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, , *Gaussian 09 Rev. D.01*, Gaussian, Inc., Wallingford CT, **2009**.

[17] T. Michinobu, C. Boudon, J.-P. Gisselbrecht, P. Seiler, B. Frank, N. N. P. Moonen, M. Gross, F. Diederich, *Chem. Eur. J.* **2006**, *12*, 1889–1905.

[18] a) J. Roose, S. Achermann, O. Dumele, F. Diederich, *Eur. J. Org. Chem.* **2013**, 3223–3231; b) N. J. Schuster, R. I. Hernández Sánchez, D. Bukharina, N. A. Kotov, N. Berova, F. Ng, M. L. Steigerwald, C. Nuckolls, *J. Am. Chem. Soc.* **2018**, *140*, 6235-6239; c) M. Milton, N. J. Schuster, D. W. Paley, R. Hernández Sánchez, F. Ng, M. L. Steigerwald, C. Nuckolls, *Chem. Sci.* **2019**, *10*, 1029–1034.

[19] H. B. Klevens, J. R. Platt, W. C. Prize, *J. Chem. Phys.* **1949**, *17*, 466–469.

[20] C. Würth, M. Grabolle, J. Pauli, M. Spieles, U. Resch-Genger, *Nat. Protoc.* **2013**, *8*, 1535–1550.

[21] a) G. Snatzke, *Angew. Chem. Int. Ed.* **1979**, *18*, 363–377; *Angew. Chem.* **1979**, *91*, 380–393; b) Y. Nakai, T. Mori, Y. Inoue, *J. Phys. Chem. A* **2012**, *116*, 7372–7385; c) T. Hosokawa, Y. Takahashi, T. Matsushima, S. Watanabe, S. Kikkawa, I. Azumaya, A. Tsurusaki, K. Kamikawa, *J. Am. Chem. Soc.* **2017**, *139*, 18512–18521; d) A. Bedi, L. J. W. Shimon, O. Gidron, *J. Am. Chem. Soc.* **2018**, *140*, 8086–8090.

[22] G. R. Seely, *J. Phys. Chem.* **1969**, *73*, 125–129.

[23] H. Sakai, S. Shinto, J. Kumar, Y. Araki, T. Sakanoue, T. Takenobu, T. Wada, T. Kawai, T. Hasobe, *J. Phys. Chem. C* **2015**, *119*, 13937–13947.

[24] a) N. Fuentes, A. Martin-Lasanta, L. Alvarez de Cienfuegos, R. Robles, D. Choquesillo-Lazarte, J. M. García-Ruiz, L. Martínez-Fernández, I. Corral, M. Ribagorda, A. J. Mota, D. J. Cárdenas, M. C. Carreño, J. M. Cuerva, *Angew. Chem. Int. Ed.* **2012**, *51*, 13036–13040; *Angew. Chem.* **2012**, *124*, 13213–13217; b) S. P. Morcillo, D. Miguel, L. Álvarez de Cienfuegos, J. Justicia, S. Abbate, E. Castiglioni, C. Bour, M. Ribagorda, D. J. Cárdenas, J. M. Paredes, L. Crovetto, D. Choquesillo-Lazarte, A. J. Mota, M. C. Carreño, G. Longhi, J. M. Cuerva, *Chem. Sci.* **2016**, *7*, 5663–5670; c) P. Reiné, J. Justicia, S. P. Morcillo, S. Abbate, B. Vaz, M. Ribagorda, Á. Orte, L. Álvarez de Cienfuegos, G. Longhi, A. G. Campaña, D. Miguel, J. M. Cuerva, *J. Org. Chem.* **2018**, *83*, 4455–4463.

[25] G. Muller, in *Luminescence of Lanthanide Ions in Coordination Compounds and Nanomaterials*, Wiley, West Sussex, **2014**, pp. 77–123.

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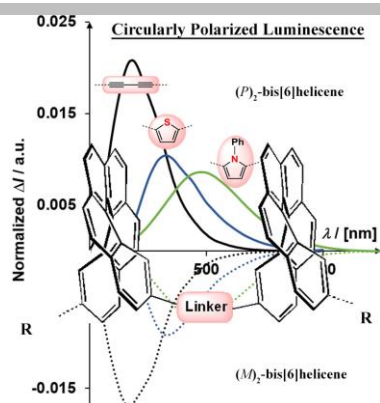
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