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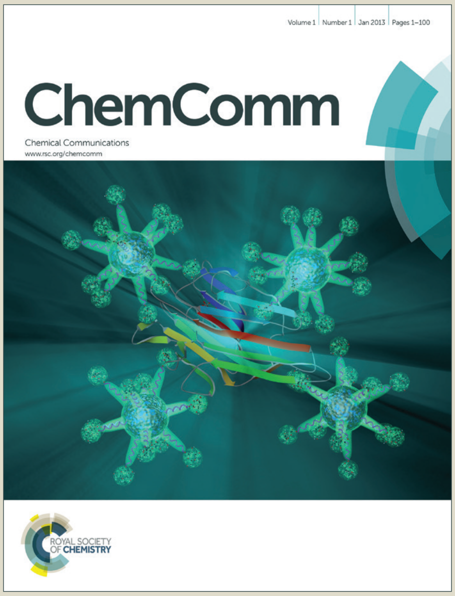

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Tetrahydro[5]helicene-based imide dyes with intense fluorescence in both solution and solid state

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A new kind of tetrahydro[5]helicene-based imide dyes with intense fluorescence and large Stokes shifts in both solution and solid state were developed and theoretically investigated.

Organic dyes with intense fluorescence, especially in the solid state,[1] have received considerable attention for their wide applications in optoelectronic materials,[2] biological sensors,[3] and fluorescence imaging.[4] Although a number of organic dyes with strong emission in solution have been reported, most of them quenched in solid state mainly owing to the aggregation and intermolecular interaction. Consequently, several strategies including the introduction of bulky substituents,[5] enhanced intramolecular charge transfer transition,[6] J-aggregated formation,[7] and aggregation-induce emission[8] have been developed to obtain intense fluorescence in the solid state. However, the systems of organic dyes with intense fluorescence in both solution and solid state are still limited, and the development of new organic dyes, especially, the solid-state fluorescence dyes is very attractive and important.

Helicene derivatives[9] are a class of polycyclic arenes with non-planar structures, so they could show intense fluorescence not only in solution, but also in solid state. However, few studies on the photophysical properties of helicene and its derivatives in solution, especially in solid state, were carried out.[10] Herein, we report a new kind of organic imide dyes based on tetrahydro[5]helicene core. By the combination of the conjugative effect, strong intramolecular push−pull electronic effect, and twist structure (Fig. 1), the dyes show intense fluorescence and large Stokes shifts in both solution and solid state. Interestingly, an expanded π-conjugated system by introducing only two phenyl groups to the hydro[5]helicene core can result in an increase of more than 14 times of the quantum yield compared with its precursor, which was theoretically explained by the investigation of emission and internal conversion rates in the framework of thermal vibration correlation function formalism.[11]

Synthesis of organic dyes **5-8** was depicted in Scheme 1. Compound **3** was first synthesized in 68% yield by the amidation reaction of **1**[4a, 12] with propyl amine. Similarly, the dibromo-substituted lactim **4** was obtained in 77% yield by the reaction of **2**[12] with dodecyl amine. Then, the Suzuki reaction of **4** with appropriate arylboronic acids gave the tetrahydro[5]helicene based dyes **5-8** in moderate to good yields.

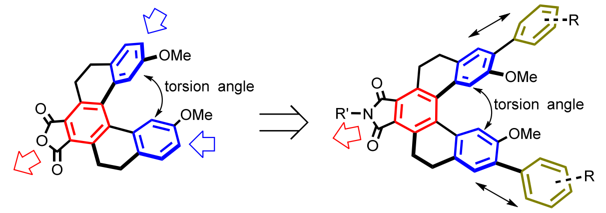
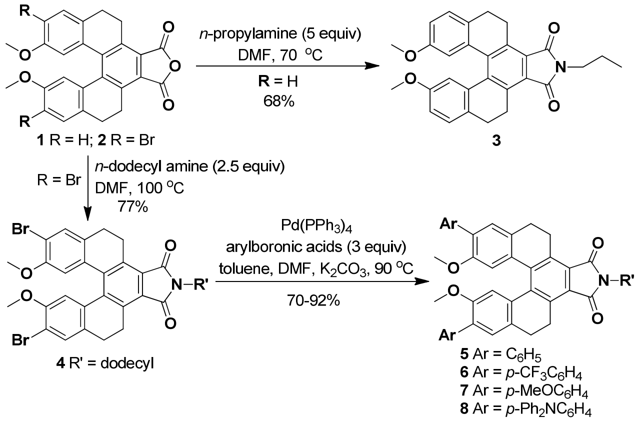


Fig. 1 Design of tetrahydro[5]helicene based imide dyes.



Scheme 1. Synthesis of compounds **3**-**8**.

The new compounds were all characterized by ^{1}H NMR, ^{13}C NMR and mass spectra. Moreover, we also obtained the single crystal of **3** suitable for X-ray analysis by its slow evaporation in CH_2Cl_2 and petroleum ether. As shown in Fig. 2, **3** showed a significantly twisted structure with the torsion angle of C10-C9-C28-C27 of 54.0°. Moreover, molecule **3** could also pack into a herringbone-like structure with the alternating left-handed and right-handed configuration molecules by C-H$\cdots\pi$ interactions (Figure S1).

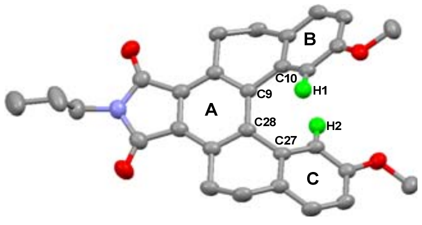


Fig. 2. Crystal structure of **3**. Hydrogen atoms were omitted for clarity.

Absorption and emission spectra of **3** and **5** in CH_2Cl_2 were shown in Fig. 3 and Table S2. Although the molar absorptivity of **5** ($\log \varepsilon$ = 4.31) is similar to that of **3** ($\log \varepsilon$ = 4.30), the maximum absorption band of **5** at 385 nm showed a red shift of 11 nm compared to **3** (374 nm) due to the large conjugated π-system of **5**. In the fluorescent spectra, the maximum emission wavelength of **5** was observed at 502 nm, which is 28 nm longer than that of **3**. It was interestingly found that both **3** and **5** exhibited a large Stokes shift of even up to 100 nm. Especially, the quantum yield of **5** (70.3 %) was found to be 14 times higher than that of **3** (4.9 %). The introduction of two phenyl groups exhibited a subtle effect on the absorption but a marked effect on the emission spectra, which is probably due to the difference between the structures in the excited state and ground state. The different structures of **5** between the ground state and excited state could also be evidenced by the solvent effect, in which the absorption spectra of **5** show only slightly solvatochromism [λ_{abs} = 380 (cyclohexane), 385 (toluene), 385 (CH_2Cl_2), 382 (THF)], but marked solvent effect was observed in the emission spectra [λ_{em} = 456 (cyclohexane), 474 (toluene), 502 (CH_2Cl_2), 483 (THF)]. It was also found that the quantum yields of **5** in the above different solutions range from 43.5% to 70.3%.

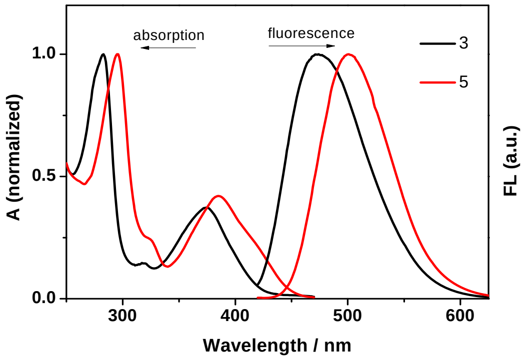


Fig. 3 UV-Vis absorption and fluorescence spectra of **3** and **5** in CH_2Cl_2.

In order to investigate the effect of the terminal two benzene rings on the photophysical properties of **5**, we theoretically studied the Stokes shift and quantum yields of **3** and **5**. The optimizations of ground state S0 and first excited state S1, and the calculations of frequency and nonadiabatic coupling matrix elements (NACMEs) were carried out with B3LYP/6-31G** method in TURBOMOLE 6.4 package.[13] Then the spectra, emission and IC rates were calculated with our home-built package. As the transition density between S1 and S0, represented in Fig. 4(c), the phenyls increased the conjugation length along *y* direction. As the result (Table S5), the transition dipole moment of **5** (5.12 Debye), calculated at the equilibrium geometry of S1, was 1.67 times larger than that of **3** (3.07 Debye), which enhanced the emission rate from 1.74×10^{7} s^{-1} to 4.04×10^{7} s^{-1}. In addition, the phenyl groups in **5** reduced the reorganization energy (see Figure S2, S3, Table S3)[14] and the Duschinsky rotation effect (DRE, Figure S4, Table S4),[15] which made the IC rate of **5** (4.82×10^{8} s^{-1}) lower than **3** (3.13×10^{9} s^{-1}). From the above, the increase of conjugation length and molecular rigidity, the quantum yield of **5**, 7.73%, was about 14 times larger than that of **3**, 0.553%. The theoretical IC rates are higher and result in small quantum yields compared with the experiment. This is due to lack of anharmonic effect in the present theory, which is hard to deal with. But the tendency of theoretical quantum yields is in accordance with the experiment.

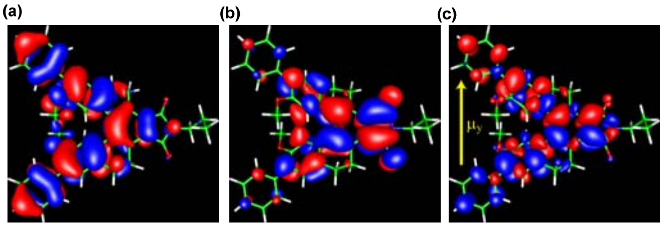


Fig. 4 The HOMO (a), LUMO (b), and transition density (c) between S_1 and S_0 of **5**.

The absorption and fluorescence spectra calculated at 300K with and without DRE of **3** and **5** were shown in Figure S6. Broadened by DRE, the second peaks of the spectra become larger than the first ones, which resulted in large Stokes shift. The normal modes contributed to the fundamental peaks were shown in Figure S7. The second and third peaks were characterized by the C-O bond stretching vibration.

Notably, **5** exhibited intense fluorescence not only in solution, but also in solid state. As shown in Figure S9, the spin-coated film of **5** showed a maximum emission band at 502 nm with a high quantum yield (Φ_f = 51%), indicating that no aggregation in either the ground state or excited state existed, which may be attributed to the twisty molecular structure that effectively suppresses the intermolecular π-π stacking. Moreover, it was also found that compared with its precursor **3** in solid state (see ESI), dye **5** with the introduction of two phenyl groups showed not only the red shift of emission wavelength, but also obvious enhancement of the quantum yield, which are consistent with the results in solution as well.

Table 1. The photophysical properties of dyes **5-8**

Compd[a]		Absorption $\lambda_{abs}{}^{b}$/nm ($\log\varepsilon$)	Fluorescence $\lambda_{em}{}^{c}$/nm ($\Phi_f{}^{d}$/%)	Stokes shift (nm)	Lifetime τ/ns
5	CH_2Cl_2	385 (4.31)	502 (70.3)	115	7.53
	film[e]	390	502 (51.0)	112	8.76
6	CH_2Cl_2	384 (4.37)	485 (46.3)	100	4.65
	film[e]	387	493 (56.6)	106	8.40
7	CH_2Cl_2	390 (4.33)	526 (85.3)	136	8.81
	film[e]	395	518 (61.8)	123	9.26
8	CH_2Cl_2	407 (4.64)	595 (7.1)	188	1.09
	film[e]	440	556 (67.3)	116	12.09

[a] Photophysical properties in CH_2Cl_2 were recorded at room temperature ($c = 1.0 \times 10^{-5}$ M). [b] Only the longest absorption maxima were shown. [c] Excited at the longest absorption maxima. [d] Absolute fluorescence quantum yield, measured by Hamamatsu Photonics Quantaurus QY. [e] Spincoated film prepared from a CH_2Cl_2 solution.

Similarly, dyes **6**, **7** and **8** with different substituents also exhibited intense fluorescence in solid state. As shown in Table 1, compared with **5**, dye **6** with two *p*-trifluoromethylphenyl groups showed a blue-shift emission at 493 nm with a quantum yield of 56.6%, while dye **7** containing two electron donating *p*-methoxyphenyl groups exhibited a red-shift emission at 518 nm with the quantum yield of 61.8%. For dye **8** with two stronger electron donating triphenyl amine groups, further red-shift emission (556 nm) and a high quantum yield (67.3%) were observed. Similar to those ones in solid state, dyes **6** and **7** also showed intense fluorescence in CH_2Cl_2 solution. By contrast, dye **8** showed weak fluorescence in CH_2Cl_2 (595 nm, 7%), which might be due to the interaction of chlorine atom and the lone electron pairs on the nitrogen. But intense fluorescence of **8** in other solutions (cyclohexane: 501 nm, 76.6%; toluene: 533 nm, 68.5%; THF: 568, 30.3%) could be observed. Moreover, it was also found that the Stokes shifts of **6-8** in both solution and solid state were all more than 100 nm. Thus, the above photophysical properties of dyes **5-8** revealed that the intense fluorescence in both solution and solid state, and the large Stokes shifts could be the general properties for the organic imide dyes based on the aryl substituted tetrahydro[5]helicene derivatives.

In conclusion, we have developed a new class of organic dyes based on tetrahydro[5]helicene core, and found that they exhibited intense fluorescence and large Stokes shifts in both solution and solid state. Especially, the quantum yield of **5** with the introduction of only two phenyl groups showed 14 times higher than its precursor **3**. Theoretical calculation revealed that the high quantum yield of **5** might be attributed to the longer conjugation length and more rigid structure, and large Stokes shifts of the dyes came from large DRE. We believe that this new kind of organic dyes could find wide potential applications in luminescent materials, fluorescent probes and biological imaging, which are in progress in our laboratory.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis and characterization data of new compounds. Theoretical calculation for **3** and **5**. UV/Vis and fluorescene spectra for **5-8**. X-ray crystallographic file for complex **3**. For the ESI and crystallographic data in CIF, see DOI: 10.1039/b000000x/

1. (*a*) C.-H. Zhao, Y.-H. Zhao, H. Pan and G.-L. Fu, *Chem. Commun.*, 2011, **47**, 5518; (*b*) D. Zhang, Y. Wen, Y. Xiao, G. Yu, Y. Liu and X. Qian, *Chem. Commun.*, 2008, 4777; (*c*) M.-J. Lin, A. J. Jimenez, C. Burschka and F. Wurthner, *Chem. Commun.*, 2012, **48**, 12050; (*d*) M. Shimizu, Y. Takeda, M. Higashi and T. Hiyama, *Angew. Chem. Int. Ed.*, 2009, **48**, 3653; (*e*) Z. Zhang, B. Xu, J. Su, L. Shen, Y. Xie and H. Tian, *Angew. Chem. Int. Ed.,* 2011, **50**, 11654; (*f*) C.-H. Zhao, A. Wakamiya, Y. Inukai and S. Yamaguchi, *J. Am. Chem. Soc.*, 2006, **128**, 15934; (*g*) C. Yuan, S. Saito, C. Camacho, S. Irle, I. Hisaki and S. Yamaguchi, *J. Am. Chem. Soc.*, 2013, **135**, 8842; (*h*) A. Wakamiya, K. Mori and S. Yamaguchi, *Angew. Chem. Int. Ed.*, 2007, **46**, 4273; (*i*) X. Feng, J.-Y. Hu, F. Iwanaga, N. Seto, C. Redshaw, M. R. J. Elsegood and T. Yamato, *Org. Lett.*, 2013, **15**, 1318; (*j*) D. Zhao, J. Hu, N. Wu, X. Huang, X. Qin, J. Lan and J. You, *Org. Lett.*, 2011, **13**, 6516-6519.
2. (*a*) T. P. I. Saragi, T. Spehr, A. Siebert, T. Fuhrmann-Lieker and J. Salbeck, *Chem. Rev.*, 2007, **107**, 1011; (*b*) Y. S. Zhao, H. Fu, A. Peng, Y. Ma, Q. Liao and J. Yao, *Acc. Chem. Res.*, 2009, **43**, 409; (*c*) T. Qin, W. Wiedemair, S. Nau, R. Trattnig, S. Sax, S. Winkler, A. Vollmer, N. Koch, M. Baumgarten, E. J. W. List and K. Müllen, *J. Am. Chem. Soc.*, 2011, **133**, 1301; (*d*) W. Z. Yuan, Y. Gong, S. Chen, X. Y. Shen, J. W. Y. Lam, P. Lu, Y. Lu, Z. Wan, R. Hu, N. Xie, H. S. Kwok, Y. Zhang, J. Z. Sun and B. Z. Tang, *Chem. Mater.*, 2012, **24**, 1518; (*e*) S. Schmidbauer, A. Hohenleutner and B. König, *Adv. Mater.*, 2013, **25**, 2114; (*f*) C. Li and H. Wonneberger, *Adv. Mater.*, 2012, **24**, 613.
3. (*a*) L. Yuan, W. Lin, K. Zheng, L. He and W. Huang, *Chem. Soc. Rev.*, 2013, **42**, 622; (*b*) L. Wang, Y. Xiao, W. Tian and L. Deng, *J. Am. Chem. Soc.*, 2013, **135**, 2903; (*c*) W. Piao, S. Tsuda, Y. Tanaka, S. Maeda, F. Liu, S. Takahashi, Y. Kushida, T. Komatsu, T. Ueno, T. Terai, T. Nakazawa, M. Uchiyama, K. Morokuma, T. Nagano and K. Hanaoka, *Angew. Chem. Int. Ed.*, 2013, DOI: 10.1002/anie.201305784.
4. (*a*) M. Li, H.-Y. Lu, R.-L. Liu, J.-D. Chen and C.-F. Chen, *J. Org. Chem.*, 2012, **77**, 3670; (*b*) H. J. Kim, C. H. Heo and H. M. Kim, *J. Am. Chem. Soc.*, 2013, **135**, 17969; (*c*) W. Sun, J. Fan, C. Hu, J. Cao, H. Zhang, X. Xiong, J. Wang, S. Cui, S. Sun and X. Peng, *Chem. Commun.*, 2013, **49**, 3890.
5. (*a*) A. Iida and S. Yamaguchi, *Chem. Commun.*, 2009, 3002; (*b*) H. Langhals, O. Krotz, K. Polborn and P. Mayer, *Angew. Chem. Int. Ed.*, 2005, **44**, 2427; (*c*) Y.-T. Lee, C.-L. Chiang and C.-T. Chen, *Chem. Commun.*, 2008, 217; (*d*) T. Qin, G. Zhou, H. Scheiber, R. E. Bauer, M. Baumgarten, C. E. Anson, E. J. W. List and K. Müllen, *Angew. Chem. Int. Ed.*, 2008, **47**, 8292; (*e*) J. M. Lupton, L. R. Hemingway, I. D. W. Samuel and P. L. Burn, *J. Mater. Chem.*, 2000, **10**, 867.
6. (*a*) C.-H. Zhao, A. Wakamiya and S. Yamaguchi, *Macromolecules*, 2007, **40**, 3898; (*b*) C.-H. Zhao, E. Sakuda, A. Wakamiya and S. Yamaguchi, *Chem.–Eur. J.*, 2009, **15**, 10603;
7. T. E. Kaiser, H. Wang, V. Stepanenko and F. Würthner, *Angew. Chem. Int. Ed.*, 2007, **46**, 5541.
8. (*a*) W. Z. Yuan, P. Lu, S. Chen, J. W. Y. Lam, Z. Wang, Y. Liu, H. S. Kwok, Y. Ma and B. Z. Tang, *Adv. Mater.*, 2010, **22**, 2159; (*b*) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361.
9. (*a*) Y. Shen and C.-F. Chen, *Chem. Rev.*, 2011, **112**, 1463; (*b*) M. Gingras, *Chem. Soc. Rev.*, 2013, **42**, 968.
10. (*a*) H. Oyama, K. Nakano, T. Harada, R. Kuroda, M. Naito, K. Nobusawa and K. Nozaki, *Org. Lett.*, 2013, **15**, 2104; (*b*) Y. Sawada, S. Furumi, A. Takai, M. Takeuchi, K. Noguchi and K. Tanaka, *J. Am. Chem. Soc.*, 2012, **134**, 4080; (*c*) Z. Y. Wang, E. K. Todd, X. S. Meng and J. P. Gao, *J. Am. Chem. Soc*., 2005, **127**, 11552; (*d*) A. Rajapakse and K. S. Gates, *J. Org. Chem*., 2012, **77**, 3531
11. (*a*) S. H. Lin, *J. Chem. Phys.*, 1966, **44**, 3759; (*b*) A. M. Mebel, M. Hayashi, K. K. Liang, S. H. Lin, *J. Phys. Chem. A*, 1999, **103**, 10674; (*c*) Q. Peng, Y. Yi, Z. Shuai and J. Shao, *J. Chem. Phys.*, 2007, **126**, 114302; (*d*) Q. Peng, Y. Yi, Z. Shuai and J. Shao, *J. Am. Chem. Soc.*, 2007, **129**, 9333; (*e*) Y. Niu, Q. Peng and Z. Shuai, *Sci. China Ser. B-Chem.*, 2008, **51**, 1153; (*f*) Y. Niu, Q. Peng, C. Deng, X. Gao and Z. Shuai, *J. Phys. Chem. A*, 2010, **114**, 7817.
12. H. S. Blair, M. Crawford, J. M. Spence and V. R. Supanekar, *J. Chem. Soc.*, 1960, 3313.
13. TURBOMOLE V6.4 2012, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.
14. J. R. Reimers *J. Chem. Phys.*, 2001, **115**, 9103.
15. F. Duschinsky, *Acta Physicochim. (USSR)*, 1937, **7**, 551.