Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2017, **27**, 268–270

Mendeleev Communications

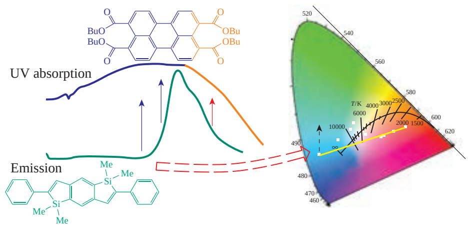
Asymmetric energy transfer results in color coordinate shift

De-bo Zhou,*[a,b] Xiao-xiao Li,[a] Kai Feng,[a] Sheng-yu Feng[a,b] and Lian-feng Wu*[c]

[a] *Key Laboratory of Special Functional Aggregated Materials, Ministry of Education; School of Chemistry and Chemical Engineering, Shandong University, 250100 Jinan, P. R. China. E-mail: bowenzhoudebo@126.com*
[b] *National Engineering Research Centre for Colloidal Materials, Shandong University, 250100 Jinan, P. R. China*
[c] *State Key Lab of Marine Coatings, Marine Chemical Research Institute Co., Ltd., 266071 Qingdao, P. R. China. E-mail: wulianfeng126@126.com*

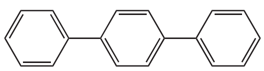
DOI: 10.1016/j.mencom.2017.05.017

Asymmetric energy transfer in white fluorescent mixtures results in fluorescence peak and color coordinate shift.

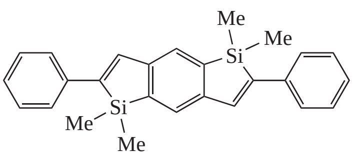


In recent years, white-light-emitting materials have been extensively investigated due to their potential applications in backlighting, lasers, indicators, and displays.[1–3] White light is composed of a variety of colors and comprises at least two colors. One chromophore functional group engenders only single color light. Thus, white-light-emitting materials should contain two or more chromophores. Inorganic white-light materials are composed of two or more materials. Similarly, organic white-light materials are composed of two or more materials or contain two or more chromophore groups in one material. To obtain white-light materials, it is necessary to mix luminescent materials with different colors at suitable proportions.[1,4] All mixed materials and single materials contain different chromophore groups in specific ratio.[5,6] Mixing various dilute solutions is a conventional method to fabricate white fluorescent material. The method prevents aggregation. However, compared with the fluorescence in solution a red shift is usually observed in solid fluorescent materials. Since fluorescent materials are generally applied in the solid state, a study of the mixed solid state materials is important.

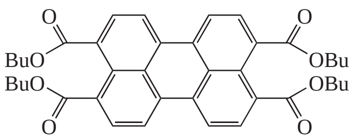
In this study, the optical behavior of the mixtures of each pair of three compounds [1,4-diphenylbenzene **1**, 1,5-dihydro-1,1,5,5-tetramethyl-2,6-diphenyl-1,5-disila-s-indacene **2**, and 3,4,9,10-(tetrabutoxycarbonyl)perylene **3**] was investigated. Compound **1** was purchased from Aladdin (China), compound **2** was synthesized in this work,[†] and compound **3** was prepared according to published procedure.[7] The solid mixtures were obtained through mixed solution flash evaporation.



1



2



3

Compound **2** possesses strong fluorescence not only in the dilute solution, but also in the solid solution. The molecule of **2** has a highly coplanar π-conjugated framework, and the dihedral angles between the central benzene plane and the outer benzene planes are both 6.60°.[8,9] The fluorescence quantum yield of compound **3** is high, and the films could be formed from this compound.[10,11] Compounds **2** and **3** are also excellent alternative materials for organic light emitting diodes or chromophores for white-light-emitting materials.

Compounds **1** and **2** emit at 406 and 475 nm, respectively. Their UV-VIS absorption peaks are at 430 and 480 nm, respectively (Figure 1). The emission of **1** is covered by the UV absorption of **2** or **3**. However, the fluorescence spectrum of **2** is asymmetric. It is covered by the UV absorption of **3**. The asymmetric absorption of **3** results in the red-shift of the fluorescence emission peaks of **2** (FEP-**2**).

The fluorescence emission spectra of the mixtures of compounds **2** and **3** are shown in Figure 2. When the ratio **2** : **3** is less than 0.75, the wavelength of FEP-**2** increases with raising the

[†] UV-VIS spectra were recorded using a Purkinje general double beam UV-VIS spectrophotometer (TU-1901). Fluorescence spectra were recorded using a Hitachi F-7000 fluorescence spectrophotometer.

Synthesis of compound **2**. Chlorotributylstannane was vigorously stirred with Li granules at 0 °C for 0.5 h, followed by sonication at 0 °C for 5 h. After evaporation of the solvents *in vacuo*, diethyl ether (1.0 ml) and 2,5-bis(dimethylsilyl)-1,4-bis(phenylethynyl)benzene were added, and the red mixture obtained was stirred for 8 h at room temperature until the mixture gradually turned green. The reaction mixture was quenched with aqueous ammonium chloride.[12] The organic layer was extracted by light petroleum, filtered, and a blue solid obtained was recrystallized from diethyl ether to yield 202 mg (90%) of compound **2**. ^{1}H NMR (300 MHz, acetone-d_6) δ: 0.51 (s, 12 H), 7.23–7.28 (m, 2 H), 7.36–7.42 (t, 4 H), 7.57–7.60 (m, 4 H), 7.63 (s, 2 H), 7.71 (s, 2 H).[9]

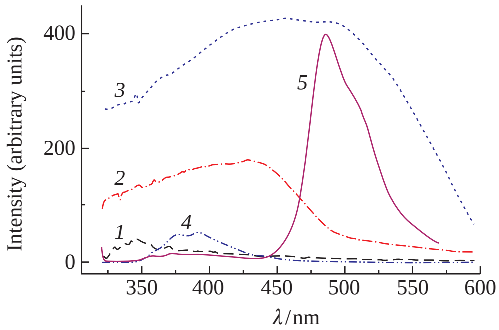


Figure 1 UV-VIS absorption spectra of (*1*) **1**, (*2*) **2**, (*3*) **3**; fluorescence emission spectra of (*4*) **1** and (*5*) **2** in solid state.

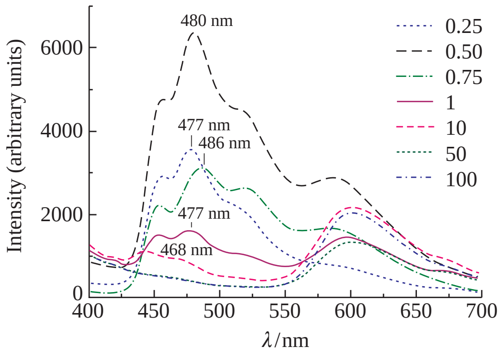


Figure 2 Fluorescence emission spectra (excitation at 365 nm) of mixtures of **2** and **3** in different ratio. The number at the line is the **3**:**2** ratio.

content of **2** in the mixture. When the ratio **2**:**3** is more than 0.75, the wavelength of FEP-**2** decreases with raising the content of **2** in the mixture.

CIE color coordinates (CIE-CC) were calculated from the emission spectra (Figure 3). The CIE-CC of fluorescence emission of the mixture of different ratio **1**:**2** or **1**:**3** excited at 290 nm were on a straight line through the CIE-CC of **1** and **2** or of **1** and **3**, respectively.

The CIE-CC of fluorescence emission of the mixture of different **2**:**3** ratio excited at 365 nm deviated from the straight line through the CIE-CC of **2** and **3**. Given that the excitation wavelength range of **3** comprises the fluorescence emission wavelength range of **2**, energy transfer occurs. This results in the shift of the color coordinates of **2**. The UV absorption peak of **3** was closer to the FEP-**2**, the absorption on the short-wavelength side being stronger than that on the long-wavelength side (see Figure 1). The short-wavelength side (<477 nm) of the fluorescence emission of **2** was more absorbed as compared with the long-wavelength side (>477 nm). Given that the fluorescence emission of **2** was asymmetrically absorbed by **3**, the red-shift of FEP-**2** occurred, and the color coordinate moved to the green region.

In the case of a high content of **3** in the mixture, the fluorescence emission of **2** was mostly absorbed by **3** regardless of whether the wavelength was short or long. The reduction of the fluorescence emission of **2** was evidently balanced. Thus, the red-shift of FEP-**2** did not occur. The color coordinates of the mixtures were nearly on the straight line through the CIE-CC of **2** and **3**. In the case of a low content of **3** in the mixture, the fluorescence of **2** was hardly absorbed by **3**. Thus, the CIE-CC of the mixtures was also nearly on the straight line through the CIE-CC of **2** and **3**. When the short-wavelength fluorescence of **2** was absorbed completely by **3**, the long-wavelength fluorescence increased with the increase in the content of **2** in the mixture. The asymmetry of fluorescence emission of **2** absorbed by **3** is enhanced and the red-shift of FEP-**2** would further occur. When the short-wavelength side of the fluorescence emission of **2** was not absorbed completely, it would increase with the growth of the content of **2** in the mixture and the red-shift of FEP-**2** would occur less likely.

When the **2**:**3** ratio was 1:1, the CIE-CC (x, y) was (0.3061, 0.3015), which is close to the standard white-light emission and may be promising for white-light-emitting devices. The straight line through the CIE-CC of **2** and **3** did not pass the white-light area. However, the emission color of the mixture shifted to the white-light area due to the color coordinate shift caused by asymmetric energy transfer.

In summary, the solid fluorescence of the mixtures of each pair of compounds **1**–**3** has been investigated. The CIE-CC shift to green of the mixtures of **2** and **3** initially increased and then decreased with raising the content of **2** in the mixture. White-light emission with CIE-CC (0.3061, 0.3015) was achieved when the **2**:**3** ratio was 1:1.

This work was supported by the National Natural Science Foundation of China (grant no. 21274080) and Special Fund for Shandong Independent Innovation and Achievements Transformation (grant no. 2014ZZCX01101).

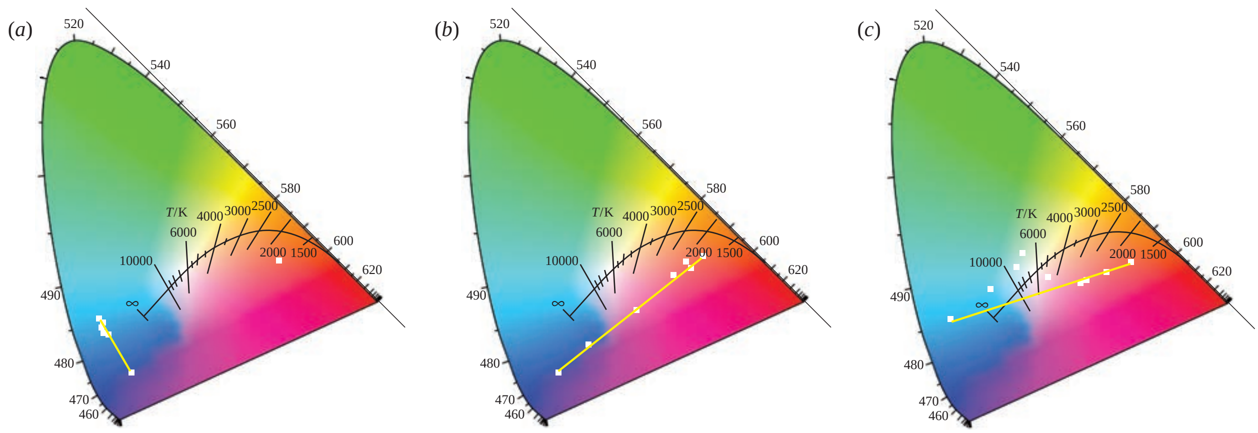


Figure 3 Emission colors of the mixtures in the CIE 1931 chromaticity diagram. Mixture of compounds (*a*) **1** + **2**, (*b*) **1** + **3**, and (*c*) **2** + **3**. Ratio and CIE color coordinates: (*a*) 4:1 (0.1388, 0.2152); 8:1 (0.1372, 0.2057); 16:1 (0.1398, 0.1917); 24:1 (0.1403, 0.2013); 32:1 (0.1411, 0.2025); 48:1 (0.1459, 0.1894); 64:1 (0.1413, 0.1924); (*b*) 1:1 (0.4891, 0.3897); 2:1 (0.5276, 0.3597); 10:1 (0.5176, 0.3661); 50:1 (0.4505, 0.3206); 100:1 (0.3736, 0.2427); and (*c*) 4:1 (0.2184, 0.2920); 2:1 (0.2764, 0.3414); 4:3 (0.2878, 0.3733); 1:1 (0.3061, 0.3015); 1:10 (0.4203, 0.3064); 1:50 (0.4279, 0.3121); 1:100 (0.471, 0.329).

References

1 G. M. Farinola and R. Ragni, *Chem. Soc. Rev*., 2011, **40**, 3467.
2 T. Fleetham and J. Li, *J. Photon. Energy*, 2014, **4**, 040991.
3 H. Dang, L.-K. Huang, Y. Zhang, C.-F. Wang and S. Chen, *Ind. Eng. Chem. Res*., 2016, **55**, 5335.
4 J. Wu, H. Zhang and S. Du, *J. Mater. Chem. C*, 2016, **4**, 3364.
5 M. Bachmann, D. Suter, O. Blacque and K. Venkatesan, *Inorg. Chem.*, 2016, **55**, 4733.
6 X. Zhuang, H. Zhang, K. Ye, Y. Liu and Y. Wang, *ACS Appl. Mater. Interfaces*, 2016, **8**, 11221.
7 S. Benning, H. S. Kitzerow, H. Bock and M. F. Achard, *Liq. Cryst.*, 2000, **27**, 901.
8 S. Yamaguchi, C. Xu, H. Yamada and A. Wakamiya, *J. Organomet. Chem.*, 2005, **690**, 5365.
9 C. Xu, A. Wakamiya and S. Yamaguchi, *Org. Lett.*, 2004, **6**, 3707.
10 S. R. Forrest, *Chem. Rev.*, 1997, **97**, 1793.
11 M. Dvorak, M. Müller, T. Knoblauch, O. Bünermann, A. Rydlo, S. Minniberger, W. Harbich and F. Stienkemeier, *J. Chem. Phys.*, 2012, **137**, 164302.
12 L. Ilies, H. Tsuji, Y. Sato and E. Nakamura, *J. Am. Chem. Soc.*, 2008, **130**, 4240.

Received: 29th August 2016; Com. 16/5033