

Luminescence Tuning and Field Effect Transistor Properties of Host-Guest Organic Semiconductor Systems

著者	李 金鵬
number	56
学位授与機関	Tohoku University
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氏名・(本籍)	り 李	じん 金	ほん 鵬
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論文審査委員	(主査)	教授	山下 正 廣
		教授	寺前 紀 夫
		教授	宇田 聡
		准教授	高石 慎 也

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Introduction

Organic Light-Emitting Field Effect Transistors (OLEFETs) have been gained much of interest in recent years for their potential application in next generation integrated devices for display, light source and integrated electronics¹⁻⁷. Comparing to the light emitting diodes, the OLEFETs could provide a way to control the recombination zone along the channel by the external electric fields. This may lead us to fundamental understanding of carrier injection, transport, and exciton recombination processes in organic semiconductors^{1,3,4,6}.

To make high performance OLEFET, it is essential to coping with two factors: (1) Ambipolar property with high carrier mobility. (2) High luminescence quantum yield. However, to achieve this aim seems to be a kind of dilemma, because the high mobility often needs strong molecular packing, but strong packing structures lead to increasing non-radiative decay paths for excitons, which cause the devices exhibit low luminescence efficiency^{2,8}. One promising way to overcome this contradiction is introducing the host-guest system. In this case, the host material can be considered as the carrier transport medium and the guest molecules act as the emitting centers which the strong packing interaction and the concentration quenching can be prevented. Some work had employed the host-guest system to investigate their FET performance and high efficiency luminescence had been observed⁸⁻¹¹.

Though the host-guest system can eliminate the concentration quenching process, it cannot significantly affect the carrier mobility in the host materials. Most of the host-guest system research work was carried out in thin film structure transistors; however, polycrystalline nature of the thin film structure often leads to relatively lower mobility. Then the possibility of the recombination process in guest molecules might be reduced by this low mobility performance. Comparing to thin film transistors, single crystal FET can provide higher mobility for carriers by reducing complex morphologies, grain boundaries and interfaces what can form traps which reduce the mobility of carriers^{12,13}. Though many efforts have been tried to get doped single crystals, few examples had been reported¹⁴. That might be due to the strict demands of the host-guest system in single crystal. Be the different shapes between the host and guest molecules will cause the lattice mismatch and the weak intermolecular interactions, and finally result in low crystal quality. To overcome these problems, one promising approach is to find suitable host and guest molecules with similar structures.

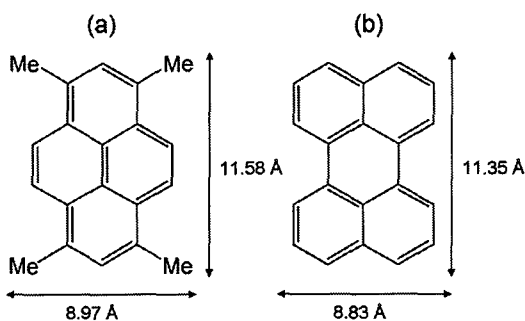


Fig. 1 Molecular structure of (a) TMPY and (b) perylene. Molecular lengths are evaluated by considering van der Waals radius of hydrogen atom (1.20 Å) and hydrogen-hydrogen distances.

Perylene is a typical luminescence material which had been investigated for several decades. It has a significant high quantum yield, about 0.94, in dilute solution. But the self-quench will happen in high concentration or pure crystal by molecular aggregation¹⁵. So it is a good candidate as a guest material. In this paper, a new molecule 1,3,6,8-tetramethylpyrene (TMPY), which has the similar shape to the renowned luminescence material perylene, has been successfully synthesized. Size of TMPY molecule is mostly same with perylene molecule (different by ca. 2 % (Fig. 1)). We use this material as the host material dope with the perylene as the luminescence centers. Now some different percentage single crystals had been grown, their luminescence performance had been characterized.

Results and Discussion

Both pure TMPY and co-single crystal belong to monoclinic, the space group is $P2_1/c$. The cell parameters of pure TMPY is $a = 11.230(6)$ Å, $b = 5.578(3)$ Å, $c = 11.275(6)$ Å, $\beta = 108.863(9)^\circ$. Comparing to pure TMPY, the co-single crystal does not change so much, the cell parameters $a = 11.1814(16)$ Å, $b = 5.6046(8)$ Å, $c = 11.1539(16)$ Å, $\beta = 109.102(3)^\circ$. From the parameters, we can find that co-single crystal nearly does not change dramatically from the pure TMPY. This indicates the similar structures of TMPY and perylene minimize the lattice mismatching in the co-single crystal. So it leads to a wide range of dope ratios. The crystal structure of the co-crystal with 13% of perylene was shown in Fig. 2, it is a typical herringbone structures which is the most common structure in planar conjugate molecules^{17,18}. The molecular position is occupied by either TMPY or perylene. To the best of my knowledge, this is the first example to solve the crystal structure of co-crystal with different molecules. The herringbone angle between the molecules in two directions is about 78.3° .¹⁹ The distance between the neighbor molecules in the same direction is 3.520 Å.

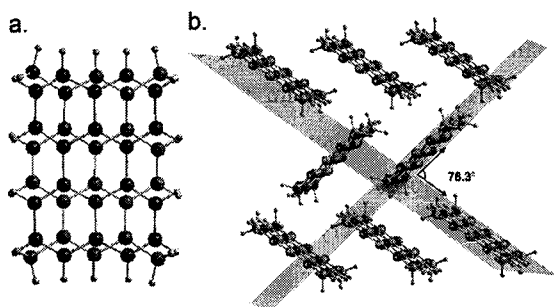


Fig. 2 (a) Molecular structure of TMPY_{0.87} Perylene_{0.13} co-crystal. (b) Herringbone packing of co-crystal and the herringbone angle of edge-to-face.

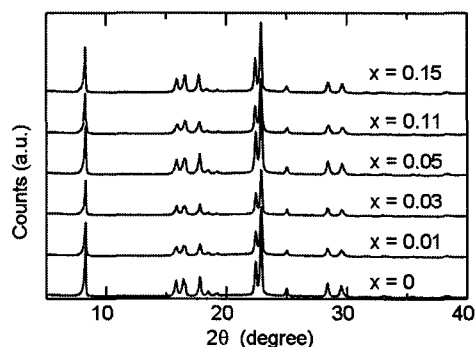


Fig. 3 PXRD pattern of TMPY_{1-x} Peryrenex co-crystals with different doping ratios.

We have confirmed that structures of TMPY_{1-x} Peryrene_x co-crystals with other doped ratio up to $x = 0.15$ are also isomorphous to pure TMPY crystal by XRPD measurements (Fig. 3).

Theoretical calculation is a good estimation about the HOMO and LUMO of molecular solid²⁰. So we put DFT calculation onto our TMPY and perylene molecules. The Fig. 4 shows the HOMO and LUMO energies of TMPY and perylene. The result shows that the TMPY molecule has a much larger energy gap than the perylene molecule. The LUMO level of TMPY is much higher than perylene. So TMPY is an ideal host material for perylene doping, because the energy transfer must be efficient from TMPY to perylene.

For better understanding the energy transfer process and luminescence performance in our co-crystal systems, we measured the solid absorption spectra of our samples (Fig 5). The solid absorption spectra of pure

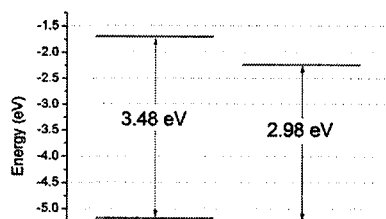


Fig. 4 DFT Calculated HOMO and LUMO levels of TMPY and Perylene.

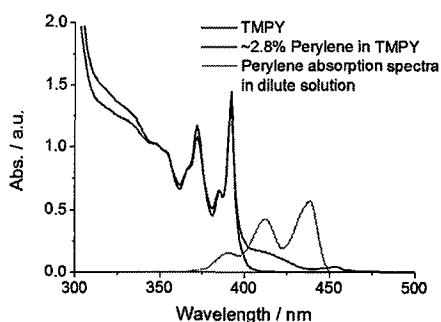


Fig. 5 The absorption spectra of pure TMPY and 2.8% doped co-crystal in solid state. And the perylene absorption spectra in dilute CHCl_3 solution.

TMPY single crystal and 2.8% co-crystal were shown that the main absorption curves of pure TMPY and co-crystal were similar below 400 nm. It can tell us the photon energy with wavelength shorter than 400 nm was mostly absorbed by the TMPY molecules. That is the main energy absorption region in our system. However, comparing with the pure TMPY, there is still some absorbance after 400 nm which was not found in the pure TMPY. The perylene molecular show its absorption around 400-450nm in diluted solution, so it is reasonable to attribute this portion to the absorption of the perylene molecules.

Fig. 6(a) shows the photoluminescence spectra of pure TMPY and doped crystals excited by 310 nm light. This exciting wavelength can insure most of the host TMPY molecules to be excited. The pure TMPY shown its luminescence peak between 400-450 nm, nevertheless the doped crystals show their emission at about 500 nm and no peak was find shorter than 450 nm. The spectra indicate that the efficient energy transfer occurred in the doped co-crystals. Furthermore, previous works announced that the main energy transfer mechanism is the Förster energy transfer in host-guest systems.^{8,9} This mechanism needs the efficient spectral overlap between the donor emission and the acceptor absorption. Checking the spectra of our system we can find that the absorbance peak of perylene measured in diluted solution (Fig. 5) was near around 400-450 nm which was also the emission area of the TMPY molecules, so there must be the significant spectra overlap between them. In addition, from the TD-DFT calculation, it has been revealed that directions of the transition dipole moment from HOMO to LUMO in TMPY and perylene are identified to be parallel to the long axis of the molecules. Coincidence of the direction is also important for the Förster energy transfer. These results convince the Förster type resonance energy transfer is the main transfer mechanism in our system. The emission spectra of different doping concentration also show the main peak has a red shift with the concentration increasing, this phenomenon can be attributed to the molecular aggregation of the guest molecules and excimer fluorescence formed in high concentration.²¹

To investigate luminescence efficiency of the doped co-crystal, the quantum yields of TMPY and co-crystals were also recorded. Fig. 6(b) shows the quantum yield of different doping concentration excited by different wavelength. From the figure we can find the quantum yield was first significant enhanced before 1% dopant concentration, near 80% quantum yield had been observed at 5% dopant concentration. This result convinces that the energy had been effective transferred from low efficiency host material to the guest material with

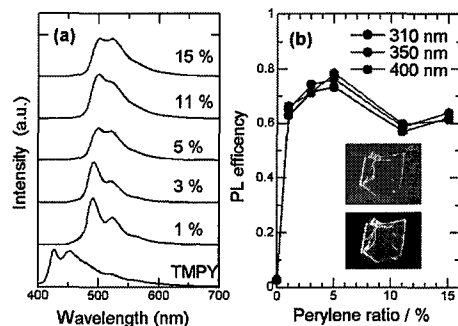


Fig. 6 (a) The luminescence spectra of pure TMPY and different doped percentages co-crystals (ex. 310 nm). (b) The PL quantum yields of TMPY and co-crystals with different exciting wavelength. Inset shows photographs of 5% doped crystal taken under visible (upper) and UV (lower) light.

high luminescence efficiency. The quantum yield in diluted solution is about 94%. In our system, the highest yield is about 78%. Since the self-quenching process is more severe in the solid state condition comparing with the diluted solution, so our system makes a good performance on luminescence efficiency. The quantum yield slowly decreases when the concentration raises up which can be attributed to the concentration quench and molecular aggregation.¹⁵

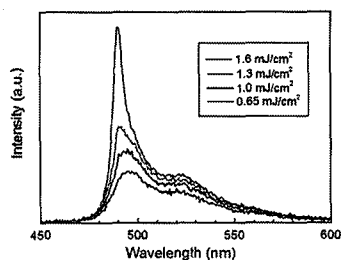


Fig. 7 Laser-pumped emission spectra of 5% doped TMPY/perylene co-crystal.

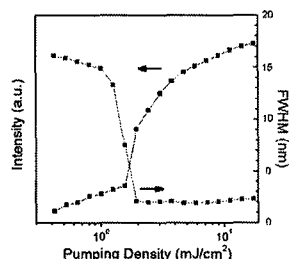


Fig. 8 Luminescence intensities and the full width at half maximum vs pumping density in the 5% doped co-crystal.

Laser-pumped emission spectra were measured on the TMPY/perylene co-single crystal, since it is an easier way to characterize the laser properties of our co-crystal.²² 5% doped sample had been used in this experiment, because we observed highest quantum yield efficiency in this concentration. Fig. 7 shows the photoemission spectra with various pump pulse intensities. Dye laser with 4,4''-bis[(2-butyloctyl)oxy]-1,1':4',1'':4'',1'''-quaterphenyl was used for pumping ($\lambda_{ex} = 385$ nm). The exciting wavelength is in the range of the absorption of TMPY molecules. The emission spectra only show the luminescence character above the 460 nm. This should be attributed to the perylene molecules emission. So the photoluminescence spectra under laser source exciting also confirm the efficient energy transfer between TMPY and perylene molecules. There is a significant narrowing trend when the pump energy promotes. Under the low pumping density at 0.65 mJ/cm², the photoluminescence spectra exhibit a broad feature above 475 nm. When the density increases, the highest peak near 490 nm has significantly enhanced. We analyzed the full width at half maximum(FWHM), and also the emission peak intensities of the emission spectra as a function of the laser intensity (Fig. 8). Following the laser intensity growth, the main peak intensities are exponentially grown accompanied by the narrowing of the FWHM. This results indicate the amplified spontaneous emission(ASE) is observed in our co-crystal systems.²³⁻²⁵ The gain-narrowing threshold was estimated to be 1.54mJ/cm² and the FWHM maintains about 2 nm above the threshold energy.

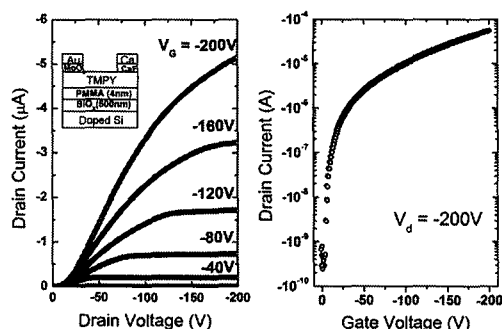


Fig. 9 Left: The FET output characteristics of the TMPY single crystal transistor for different gate voltages and the device structure(inside); Right: The transfer characteristics of the TMPY transistor at $V_d = -200V$.

For clarifying the transport properties of the TMPY crystal, we fabricated the single crystal FET device for measurement. For enhancing the carrier injection, asymmetric electrodes were used,^{3,4} and buffer layers were introduced between the electrodes and organic semiconductor. Only p-type characteristic was observed from the output characteristics (Fig. 9). The threshold voltage is -33.3V for the p-type transistor. Transfer curve shows hole mobility derived from the saturated mode is as good as $0.26\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ with the channel length and width of $18\text{ }\mu\text{m}$ and $147\text{ }\mu\text{m}$, respectively. By theoretical calculation, we got the HOMO and LUMO energy levels are -5.19 eV and -1.71 eV . Comparing with the work function of Au (-5.1 eV) and Ca (-2.87 eV), the Schottky barrier at the interface of Au electrode is much smaller than at the Ca electrode.²² Since the ambipolar FET needs both electrons and holes to be injected into the channel simultaneously from the electrodes, the high Schottky barrier at the Ca electrode is unfavorable to the ambipolar operation.

Conclusions

In the summary, we have synthesized an ideal host molecule for the doping system of high luminescence material perylene. The single crystal X-ray diffraction data convince the co-crystals have been successfully grown. The optical spectra indicate that the energy transfer has occurred in the host-guest system, the luminescence quantum yields have been enhanced by the effective energy transfer to the high quantum yield molecules. The ASE phenomena had been observed under the pulse laser excitation. The FET analysis shows that the TMPY only has unipolar operation during the gate voltage tuning. All these convince the host-guest system is a good method to fabricate the LEFET devices, and furthermore, to investigate the organic semiconductor laser performance. The future work is to investigate idea host-guest systems to make ambipolar LEFET.

References

- 1 J. Zaumseil, R. H. Friend and H. Sirringhaus., *Nat. Mater.*, 2006, 5, 69-74.
- 2 M. Muccini *Nat. Mater.*, 2006, 5, 605-613.
- 3 T. Takahashi, T. Takenobu, J. Takeya, and Y. Iwasa, *Adv. Funct. Mater.*, 2007, 17, 1623-1628.
- 4 S. Z. Bisri, T. Takenobu, Y. Yomogida, H. Shimotani, T. Yamao, S. Hotta and Y. Iwasa, *Adv. Funct. Mater.*, 2009, 19, 1728-1735.
- 5 F. Cicoira and C. Santato, *Adv. Funct. Mater.*, 2007, 17, 3421-3434.
- 6 A. Hepp, H. Heil, W. Weise M. Ahles, R. Schmechel and H. von Seggern., *Phys. Rev. Lett.* 2003, 91, 157406
- 7 R. Capelli, S. Toffanin, G. Generali, H. Usta, A. Facchetti and M. Muccini., *Nat. Mater.*, 2010, 5, 496-503
- 8 T. Oyamada, H. Uchiuzo, S. Akiyama, Y. Oku, N. Shimoji, K. Matsushige, H. Sasabe and C. Adachi., *J. Appl. Phys.*, 2005, 98, 074506.
- 9 T. Oyamada, H. Sasabe, Y. Oku, N. Shimoji and C. Adachi, *Appl. Phys. Lett.*, 2006, 88, 093514
- 10 Y. Kawamura, J. Brooks, J. J. Brown, H. Sasabe and C. Adachi, *Phys. Rev. Lett.*, 2006, 96, 017404.
- 11 H. Nakanotani, M. Saito, H. Nakamura and C. Adachi, *Advanced Functional Materials*, 2010, 20, 1610-1615
- 12 R. W. I. de Boer, M. E. Gershenson, A. F. Morpurgo and V. Podzorov, *physica status solidi (a)*, 2004, 201, 1302-1331
- 13 M. E. Gershenson, V. Podzorov and A. F. Morpurgo, *Reviews of Modern Physics*, 2006, 78, 973

- 14 H. Wang, F. Li, B. Gao, Z. Xie, S. Liu, C. Wang, D. Hu, F. Shen, Y. Xu, H. Shang, Q. Chen, Y. Ma and H. Sun, *Cryst. Growth Des.*, 2009, **9**, 4945-4950
- 15 B. X. Mi, Z. Q. Gao, C. S. Lee, S. T. Lee, H. L. Kwong and N. B. Wong, *Applied Physics Letters*, 1999, **75**, 4055-4057.
- 16 Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, 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, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- 17 M. Bendikov, F. Wudl and D. F. Perepichka, *Chem. Rev.*, 2004, **104**, 4891-4946
- 18 J. E. Anthony, *Chem. Rev.*, 2006, **106**, 5028-5048
- 19 B. Nickel, M. Fiebig, S. Schiefer, M. Göllner, M. Huth, C. Erlen and P. Lugli, *physica status solidi (a)*, 2008, **205**, 526-533
- 20 P. I. Djurovich, E. I. Mayo, S. R. Forrest and M. E. Thompson, *Organic Electronics*, 2009, **10**, 515-520
- 21 C. W. Tang, S. A. VanSlyke and C. H. Chen, *J. Appl. Phys.*, 1989, **65**, 3610-3616
- 22 M. D. McGehee and A. J. Heeger, *Adv. Mater.*, 2000, **12**, 1655-1668
- 23 M. Ichikawa, R. Hibino, M. Inoue, T. Haritani, S. Hotta, T. Koyama and Y. Taniguchi, *Adv. Mater.*, 2003, **15**, 213-217
- 24 M. D. McGehee, R. Gupta, S. Veenstra, E. K. Miller, and A. J. Heeger, *Phys. Rev. B*, 1998, **58**, 7035.
- 25 M. A. Diaz-Garcia, S. F. De Avila and M. G. Kuzyk, *Appl. Phys. Lett.*, 2002, **80**, 4486-4488.
- 26 S. Z. Bisri, T. Takahashi, T. Takenobu, M. Yahiro, C. Adachi and Y. Iwasa, *Jpn. J. Appl. Phys.*, 2007, **46**, L596-L598

論文審査の結果の要旨

本論文は、ホスト-ゲスト型の有機半導体における発光、およびトランジスタ特性の合理的設計に関する研究について述べられている。近年、有機発光トランジスタ(OLET)は有機発光ダイオードに代わるデバイスとして注目を集めている。本論文では、従来のOLETの限界を示した上で、この限界を打ち破るために、ホスト-ゲストという新しい概念・方法論を提案し、この方法論の妥当性について議論している(第一章)。

第二章では、ホスト-ゲスト分子の組み合わせとして、テトラメチルピレン(TMPY)-ペリレン系を実際に組み合わせた混合単結晶の作成をおこなった。これらの構造は単結晶X線構造解析によって明らかにし、ペリレンの比率も1~15%まで、単結晶性を保ったまま幅広く導入することが可能であることを明らかにした。

第三章では、テトラメチルピレン(TMPY)-ペリレン系の混合結晶における光学特性を詳細に調べ、混合結晶はTMPYに比べ、約26倍もの発光量子収率をしめすことを明らかにした。また、この発光効率の向上はTMPYからペリレン分子への効率的なエネルギー移動に起因していることを明らかにした。また、実際に混合結晶を用いた単結晶電界効果トランジスタデバイスを作成し、これらの混合結晶の半導体特性について評価し、これらが比較的よいp型半導体特性を示すことを明らかにした。

第四章では、理論計算等を元に、新しいホスト・ゲストの組み合わせを模索し、新たに作成したホスト-ゲスト混合結晶について、構造、光学特性を明らかにした。

第五章では、ホスト-ゲスト型の有機半導体における可能性や今後解決すべき点などについて研究全体の総括を行った。

以上の内容は、論文提出者が自立して研究活動を行うために必要な高度の研究能力と学識を有することを示している。したがって、李金鵬提出の博士論文は博士(理学)の学位論文として合格と認める。