

Bandgaps Engineering in Light-emitting Polymers via from *p-n* Diblock Copolymerization to Inorganic/Organic Hybridization

Ling-Hai Xie and Wei Huang*

Jiangsu Key Laboratory for Organic Electronics & Information Displays and Institute of Advanced Materials (IAM), Nanjing University of Posts and Telecommunications (NUPT), 9 Wenyuan Road, Nanjing 210046, China
Phone: +86 25 8586 6008, Fax: +86 25 8586 6999, Email: iamwhuang@njupt.edu.cn

Abstract

Heteroatom-containing π -conjugated *p-n* diblock copolymers, π -conjugated metallopolymers, and nanocrystal-hybridized rod-coil polymers as well as π -stacked polymers have been explored as promising new-generation materials for optoelectrical devices.

Introduction

Light-emitting materials and devices are starting for photo-information processors, transformers, chokes, transducers, sensors, and detectors as well as display and lighting sources.¹ Over the past decades, light-emitting polymers (LEPs) have attracted much attention since poly(para-phenylene vinylene) (PPV) was first reported in 1990 due to their soft-matter features as well as their high potentials and advantages in flexible and low-cost devices arising from solution processes such as spin-casting and ink-jetting.² π -Orbital interaction provide a new chance for electron delocalization, generating semiconducting or conducting features, followed by the recombination of electrons and holes from the two opposite electrodes resulting in the radiative decay of excitons. One of key issue to organic optoelectrics is to control emissive wavelength via molecular engineering when white and RGB three primary colors with high quantum-efficiency become promising techniques for next-generation flat panel displays and solid lighting sources.

In the last decades, our group focuses on exploring a series of new-concept models, including heteroatom-containing π -conjugated *p-n* diblock copolymers, π -conjugated metallopolymers, and nanocrystal-functionalized rod-coil polymers as well as π -stacked polymers, in order to effectively tune the electron, hole and exciton behaviors. In the prototype PLEDs, balanced injection and transport of electrons and holes are therefore crucial for achieving high quantum efficiency. Unfortunately, so far most of the electroluminescent polymers have unipolar character, showing greater tendency for transporting holes than for transporting electrons. To overcome the problem of the unbalanced charge injection, we present a new molecular design and synthesis, i.e., *p-n* diblock conjugated copolymers, in which typical *p*-dope type and *n*-dope type segments are alternatively incorporated into one backbone of conjugated polymer, to adjust the HOMO and LUMO of the resulting polymers.^{3,4} Their charge transfer behaviors in oxadiazole-co-oligothiophene systems offer an up to 0.5 eV range for HOMO and LUMO energy levels.^{5,6} Nearly 100% internal quantum efficiency can be achieved

because of the full utilization of singlet and triplet excitons owing to the strong spin-orbital mixing of heavy-metal ions in the complexes.⁷ Among phosphorescent heavy-metal complexes, iridium complexes have been considered as one of the best phosphorescent-material candidates because they show intense phosphorescence at room temperature and significantly shorter phosphor lifetime compared with other heavy-metal complexes, which is crucial for the performance of phosphorescent materials. Moreover, the emission color can be tuned easily over the entire visible region by modifying the structure of the ligand. Our group successfully designed and synthesized a series of π -conjugated chelating polymers that emit red light by the copolymerization of the fluorene unit and the charged Ir complex unit.^{8,9} Almost complete energy transfer from the host fluorene segments to the guest Ir complexes was achieved in the solid state when the feed ratio was 2 mol%. However in the corresponding blend system, energy transfer was not complete even when the content of Ir complexes was as high as 16 mol%. Intra- and inter-chain energy transfer mechanisms coexisted in the energy-migration process of this host-guest system, and the intramolecular energy transfer might be a more efficient process. The semiconductor nanocrystal-conjugated polymer (NC-CP) hybrid that combines the diversity of semiconducting polymers with the excellent photoelectrical properties of nanocrystals has been proved to improve the performance of optoelectronic devices. A solution-processed NCCP hybrids has been widely developed and requires control over morphology at molecular and meso-scale order.¹⁰ Our group proposed that introducing such ligands into the conjugated polymer systems would facilitate the combination of conjugated polymer and the nanocrystals. In this aspect, our group has successfully prepared the complex of PDMAEMA-PFPDMAEMA and CdSe NCs (NCs-PF) by performing a capping ligand exchange. At the same time, we have investigated the morphology of the complex. Changes in fluorescence intensity have been acting as an indicator of the electronic interaction between nanocrystals and the conjugated segments of PDMAEMA-PF-PDMAEMA.¹¹ A more effective FRET process occurred in the larger-sized QDs and polymer hybrid systems were also observed both from steady-state fluorescence spectra and time-resolved fluorescence spectra.¹²

Conclusions

Tuning redox behavior and emissive wavelength of conjugated polymers can be successfully realized by

covalently heteroatom-, coordinately metallo- and electrostatically nanocrystal-doping π -conjugated systems.

References

1. Forrest, S. R. *Nature* 2004, 428, 911-918.
2. Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature* 1999, 397, 121-128.
3. Yu, W. L.; Meng, H.; Pei, J.; Huang, W.; Li, Y. F.; Heeger, A. J. *Macromolecules* 1998, 31, 4838-4844.
4. Huang, W.; Meng, H.; Yu, W. L.; Pei, J.; Chen, Z. K.; Lai, Y. H. *Macromolecules* 1999, 32, 118-126.
5. Yu, W. L.; Meng, H.; Pei, J.; Huang, W. *Journal of the American Chemical Society* 1998, 120, 11808-11809.
6. Huang, W.; Meng, H.; Yu, W. L.; Gao, J.; Heeger, A. J. *Advanced Materials* 1998, 10, 593-596.
7. Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* 1998, 395, 151-154.
8. Liu, S. J.; Zhao, Q.; Chen, R. F.; Deng, Y.; Fan, Q. L.; Li, F. Y.; Wang, L. H.; Huang, C. H.; Huang, W. *Chemistry-a European Journal* 2006, 12, 4351-4361.
9. Liu, S. J.; Zhao, Q.; Deng, Y.; Xia, Y. J.; Lin, J.; Fan, Q. L.; Wang, L. H.; Huang, W. *The Journal of Physical Chemistry C* 2007, 111, 1166-1175.
10. Liu, S. J.; Zhao, Q.; Fan, Q. L.; Huang, W. *European Journal of Inorganic Chemistry* 2008, 2177-2185.
11. Fang, C.; Qi, X. Y.; Fan, Q. L.; Wang, L. H.; Huang, W. *Nanotechnology* 2007, 18, 035704(035701-035705).
12. Fang, C.; Zhao, B. M.; Lu, H. T.; Sai, L. M.; Fan, Q. L.; Wang, L. H.; Huang, W. *Journal of Physical Chemistry C* 2008, 112, 7278-7283.