

Photoluminescent n-type liquid organic semiconductor

Fengjun Wei (魏风军)* and Qiuli Jia (贾秋丽)

Henan University of Science and Technology, Luoyang 471023, China

*Corresponding author: wfj@mail.haust.edu.cn

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Liquid 4,7-bis(1-decynyl)-2,1,3-benzothiadiazole (DOBT) is found to exhibit good photoluminescence (PL) with high PL efficiency up to 17.8%. In particular, DOBT shows electron mobility of $5.2 \times 10^{-6} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, demonstrating a promising n-type liquid semiconductor for optoelectronic application.

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In past decades, a multitude of organic semiconducting materials have been specifically designed for research on devices such as organic light-emitting diodes^[1], organic photovoltaics^[2], organic field-effect transistors^[3], and photoreceptors^[4]. However, almost all of them are classified into the solid-state category including amorphous^[5], crystalline^[6], or semicrystalline^[7] solids. Therefore, pre-processing usually has to be carried out under high vacuum deposition^[8] or solution conditions^[9] to achieve device structures, which not only require pinpoint accuracy that actually increases difficulty in operating but also leave some unexpected defects in the active layer and the interface between organic materials and metal electrodes which finally restrict the device performance in large scale.

Recently, there have been reports regarding organic electronic devices incorporating free-flowing liquid organic semiconductors replacing conventional materials. Hopefully, the number of potential advantages of incorporating liquid semiconductors such as good interfacial contact with rough surfaces and the possibility of solvent-free (or solvent-minimal) device processing^[10] has been gradually acknowledged. However, further exploration of this unique class of materials has hampered the research on transport mechanism and application of devices. Therefore, these devices based still on liquid semiconductor are fabricated in the multi-layer and dopant-needed conformations for easy charge injection and transport.

In particular, some materials in their isotropic phases exhibited electronic transport. For instances, hexakis(hexylthio)triphenylene^[11] and 2-(4-octylphenyl)-6-*n*-butoxynaphthalene^[12], well-studied liquid crystalline materials, show hole and electron mobilities with the order of $10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Also, it has to be mentioned that both of them have been measured at high temperature above 90 °C for reaching their clear points. From the point of practical application, room temperature liquid semiconductors are required.

However, to the best of our knowledge, only two room temperature liquid semiconductors, 9-(2-ethylhexyl)carbazole^[13] and *N,N*-bis(4-(triisopropylsilyloxy)phenyl)-3,4-dimethylaniline^[14], have been prepared and

their mobilities were characterized by time-of-flight (TOF) technique. The former showed a hole mobility around $10^{-6} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ^[13] and the later showed a temperature-dependent positive charge transport mobility ranging from 10^{-7} at -20 to $10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 60 °C^[14]. But, in these two materials, no electron transport was presented at all. Empirically, there might be too much trapping sites for negative charge, probably originating from trace amount of impurities^[15].

A photoluminescent liquid, 4,7-bis(1-decynyl)-2,1,3-benzothiadiazole (DOBT) (Fig. 1), was synthesized through Sonogashira coupling between 4,7-dibromo-2,1,3-benzothiadiazole and 1-decyne according to a recent report^[16]. This compound exhibited good free fluidity at ambient temperature and strong photoluminescence (PL) even under visible light. Its PL property is also discussed in this letter. Furthermore, it was found that DOBT also showed typical negative transient photocurrent in TOF experiment, leading to an electron mobility of $5.2 \times 10^{-6} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

Figure 2 shows optical absorption, PL, and PL efficiency. In the absorption spectrum, the position of absorption maximum appeared at 461 nm resulting in a little narrow energy gap of 2.7 eV, which can be compared with those observed for large conjugation systems obtained in the solid state, such as hexabenzocoronene^[17] and perylene^[18] derivatives. PL spectra were obtained by illuminating the sample with Xe laser light of wavelength in the range between 250 and 450 nm. This PL spectrum emitted using a wavelength of 300 nm laser line almost covered visible optical region from 400 to 700 nm.

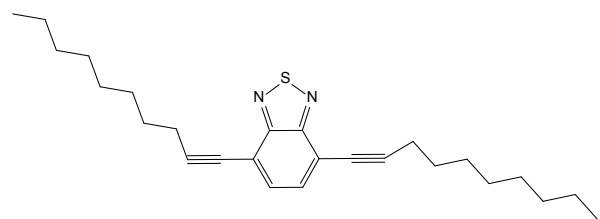


Fig. 1. Molecular structure of DOBT.

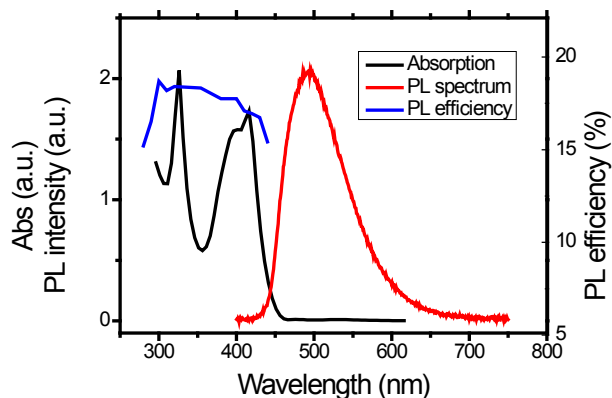


Fig. 2. Optical absorption, PL, and PL efficiency.

The PL quantum yield was measured by comparing the integration of the emission spectrum of a sample with a standard one under identical optical condition. As can be seen in Fig 2, DOBT exhibited very high PL efficiency which has been reported rarely in small organic molecule fields. Generally, the generated excitations at high photon energies relative to the onset of π - π^* absorption are particularly important for the charge generation in this kind of π -conjugated systems. The excitonic states are considered to be more delocalized when excitations generated at high photon energies, which facilitate exciton dissociation and give rise to a significant increase in the efficiency for charge generation. However, in our direct measurement, a weak dependence of PL efficiency on the excitation wavelengths was observed, which presented an arched trace with a maximum of 17.8% at 300 nm. And even at the edges of the optical absorption, a high PL efficiency of 15.3% was detected. Similar observations were reported even for a cyano derivative of poly (*p*-phenylenevinylene) (PPV)^[19], aluminum-trisquinolate^[20], and pristine PPV^[21].

To investigate n-type semiconducting property of DOBT, the transient photocurrent measurement was performed by a conventional TOF experiment^[22-24]. The TOF equipment included a nitrogen gas laser ($\lambda = 337$ nm, pulse duration time = 600 ps, power per pulse = 13.6 μ J),

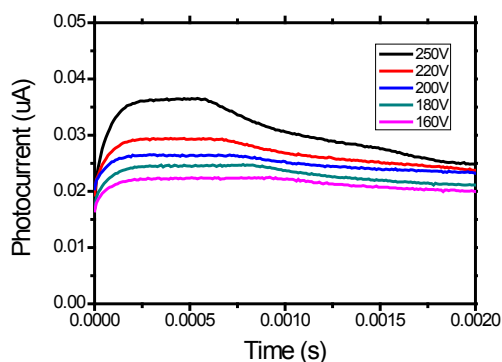


Fig. 3. Linear plot of typical transient photocurrents for negative carriers as a function of time at room temperature, the sample thickness is 9 μ m.

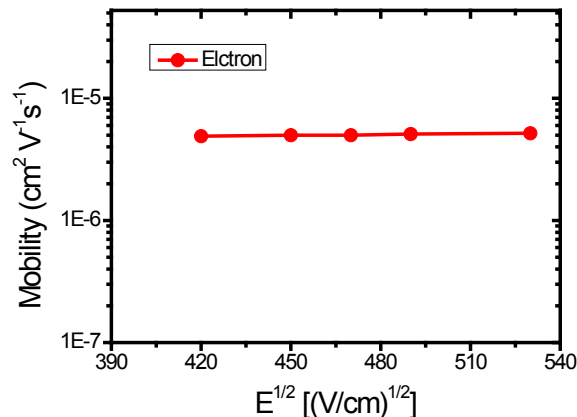


Fig. 4. Electrical field dependence of hole and electron mobilities at room temperature.

digital oscilloscope, and hot stage whose temperature was controlled by PID thermocontroller. Carrier mobility μ can be estimated from the equation $\mu = d^2/V\tau_T$, where d is the sample thickness, V is the applied voltage, and τ_T is the transit time of photogenerated carriers through the bulk sample. The τ_T was decided by kink points in double logarithmic plots of transient photocurrent as a function of time. In all the measurements, the resistance was 10000 Ω . The transient photocurrents of negative charges were gained in a non-dispersive manner (Fig. 3), which contributed to small intermolecular distance beneficial for electron hopping from one molecule to another, and also indicated excellent purity in this liquid sample^[15].

The carrier mobility in DOBT for electron was determined to be 5.2×10^{-6} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. The mobility, although quite low, is still on the same order of magnitude with those in molecularly doped polymers^[25] and triarylamine derivatives^[26] (practically used as an indispensable component of the photoreceptor for xerographic copiers and laser beam printers, respectively) and higher than that of tris(8-hydroxyquinolinolato-N1,O8) aluminum (Aq3)^[27].

In particular, the mobility can be described as $\mu \propto \exp(\beta E^{1/2})$, where β is a constant. Figure 4 shows the logarithmic mobility versus $E^{1/2}$ plot for electron mobility. It can be seen that very weak electric field dependence of electron mobility is exhibited, which points out the evidence for the involvement of ionic transport^[15]. Furthermore, the characteristic electric field-independent mobility strongly indicates very small intermolecule space in this free-fluidity liquid semiconductor, which was usually discussed only in liquid crystal materials that usually align well and self-organize into very highly ordered structures providing fast pathway for charge transport^[17,18].

In conclusion, we present a novel liquid compound with wide absorption, excellent PL, and high PL efficiency up to 17.8%. Also charge transport measurement is done through TOF, which exhibits a high electron mobility up to 5.2×10^{-6} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, almost independent

of the electric field. This new n-type photoluminescent liquid semiconductor can be promising application in flexible optoelectronics.

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References

1. S. Huang, Z. Ye, J. Lu, Y. Su, C. Chen, and G. He, *Chin. Opt. Lett.* **11**, 062302 (2013).
2. C. Brabec, U. Scherf, and V. Dyakonov, *Organic Photovoltaics: Materials, Device Physics, and Manufacturing Technologies* (Wiley-VCH, 2008).
3. S. Allard, M. Forster, and B. Souharce, *Angew. Chem. Int. Ed.* **47**, 4926 (2008).
4. P. M. Borsenberger and D. S. Weiss, *Organic Photoreceptors for Xerography* (Marcel Dekker, 1998).
5. S. Benjamin, J. K. Christof, and F. Michael, *Macromol. Rapid Commun.* **30**, 1258 (2009).
6. S. Wang, G. Jia, X. Liu, S. Chi, J. Zhu, Y. Gao, and Z. Chen, *Chin. Opt. Lett.* **10**, 041602 (2012).
7. S. Sergeev, W. Pisula, and Y. Geerts, *Chem. Soc. Rev.* **36**, 1902 (2007).
8. T. Yasuda and T. Tsutsui, *Chem. Phys. Lett.* **402**, 395 (2005).
9. J. Jou, W. Wang, and S. Chen, *J. Mater. Chem.* **20**, 8411 (2010).
10. D. Xu and C. Adachi, *Appl. Phys. Lett.* **95**, 053304 (2009).
11. D. Adam, P. Schuhmacher, and J. Simmerer, *Nature* **371**, 141 (1994).
12. M. Funahashi and J. Hanna, *Appl. Phys. Lett.* **73**, 3733 (1998).
13. S. Hirata, K. Kubota, and H. H. Jung, *Adv. Mater.* **23**, 889 (2011).
14. B. A. Kamino, T. P. Bender, and R. A. Klenkler, *J. Phys. Chem. Lett.* **3**, 1002 (2012).
15. H. Iino, Y. Takayashiki, and J. Hanna, *Appl. Phys. Lett.* **87**, 192105 (2005).
16. Y. B. Ruan, Y. Yu, and C. Li, *Tetrahedron* **69**, 4603 (2013).
17. J. Wu, M. Watson, L. Zhang, Z. Wang, and K. Müllen, *J. Am. Chem. Soc.* **126**, 177 (2004).
18. G. P. Cristina, A. Rosa, and M. A. Ana, *J. Chrom. A* **1129**, 189 (2006).
19. N. T. Harrison, D. R. Baigent, and J. Halls, *Synth. Metals* **76**, 43 (1996).
20. D. Z. Garbuzov, *Chem. Phys. Lett.* **249**, 433 (1996).
21. N. T. Harrison, G. R. Hayes, and R. T. Phillips, *Phys. Rev. Lett.* **77**, 1881 (1996).
22. H. Li, L. Duan, C. Li, L. Wang, and Y. Qiu, *Org. Electron.* **15**, 524 (2014).
23. H. Li, L. Duan, D. Zhang, and Y. Qiu, *Appl. Phys. Lett.* **104**, 183301 (2014).
24. J. C. Blakesley, M. Schubert, and R. Steyrleuthner, *Appl. Phys. Lett.* **99**, 183310 (2011).
25. R. H. Young and J. J. Fitzgerald, *J. Phys. Chem.* **99**, 4230 (1995).
26. Y. Kanemitsu, H. Funada, and Y. Masumoto, *J. Appl. Phys.* **71**, 300 (1992).
27. R. G. Kepler, P. M. Beeson, and S. J. Jacobs, *Appl. Phys. Lett.* **66**, 26 (1995).