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A soluble 5-carbazolium-8-hydroxyquinoline Al(III) complex as a dipolar luminescent material

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Abstract—A novel 8-hydroxyquinoline derivative with a carbazole group substituting in the 5-position of quinoline was synthesized, where carbazole acted as a hole transporter. The single crystal of this 8-hydroxyquinoline derivative was obtained. Its coordination complex with Al(III) was also synthesized. This complex with the ability of hole transportation and electron transportation simultaneously was soluble in common organic solvents and showed yellow luminescence with high quantum yield.

Organic light-emitting diodes (OLEDs) are currently under intensive investigation for application as a promising display technology due to their high luminous efficiency and capability of emitting full colours.[1] The devices normally consist of at least one hole-transport layer and one electron-transport layer with an organic/organic heterojunction. For OLEDs, the validity of the electron–hole recombination is directly affected by the mobilities of electrons and holes in the materials and has a great influence on the efficiency of OLEDs. To balance charge transport, attempts have also been made to incorporate electron- and hole-transport functions in the same molecule or polymer in an effort to attain maximum performance.[2] Dipolar materials featuring the combination of triarylamine–oxadiazole,[3] or triarylamine–pyridine/quinoline,[4] triarylamine–quinoxaline/oxadiazole[5,2a] were synthesized and applied in OLEDs.

About two decades have elapsed since Alq_3 (tris(8-hydroxyquinolino)aluminum) appeared as a milestone for the development of OLEDs.[6] Alq_3 is still one of the most stable and fluorescent solid-state materials, making it as the emitting material and electron-transport layer (ETL). Subsequently metaloquinolates have become a very important class of electroluminescent material in OLED.[7] Compared to its excellent capacity of electron transportation, the ability of hole transportation of Alq_3 is poor because of the presence of effective LUMO overlaps between neighbouring molecules and the absence of effective HOMO overlaps.[8] In order to obtain efficient OLEDs, the extra hole-transporter layer (HTL) is necessary besides Alq_3. Aromatic *tert*-amines are excellent hole-transporting materials.[9] For example, carbazole derivatives are widely used as hole-transporting materials between the emitting layer and the anode to balance the charge injection. Moreover, Alq_3 must be vacuum deposited in the fabrication of OLEDs due to the poor solubility of Alq_3. However, the current trend to fabricate OLEDs is solution processing. The principal interest in the use of soluble Alq_3 complex derivatives lies in the scope for low-cost manufacturing, such as spin coating.

We here designed and synthesized a new bifunctional and dipolar material which consisted of carbazole and Alq_3. The introduction of carbazole units might influence the HOMO energy level of the Alq_3 complex, tune the hole-transporting ability of the material and therefore the material would have ability of electron- and hole-transportation simultaneously. The solubility in common organic solvents and the hole mobility of the complex might be enhanced by introducing carbazole group at the 5-position of 8-hydroxyquinoline via a single bond. The photophysical properties of the complex in solution and in solid have been investigated.

Keywords: 8-Hydroxyquinline; Al(III) complex; Carbazole; Electron- and hole-transporter.

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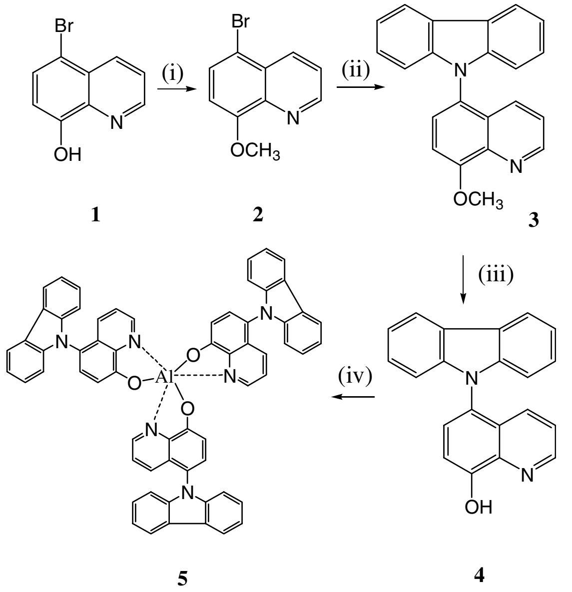

Scheme 1. Synthesis of substituted 8-hydroxyquinoine ligand and its complex with Al(III). Reagents and conditions: (i) Acetone, K_2CO_3, CH_3I, reflux; (ii) Carbazole, CuI, K_2CO_3, 18-Crown-6; (iii) HBr, CH_3COOH; (iv) $Al(NO_3)_3 \cdot 9H_2O$, ethanol, NEt_3.

The synthesis of complex **5** (Scheme 1) departs from 5-bromo-8-hydroxyquinoline **1**. Condensation of **1** with a little excess of iodomethane in the presence of K_2CO_3 gave 5-bromo-8-methoxyquinoline **2**. Intermediate **2** was coupled by Ullmann reaction with carbazole to yield **3** using CuI, K_2CO_3 and 18-crown-6 as the catalyst. Through hydrogenolytic deprotection, ligand **4** was obtained. The final Al(III) complex **5** was achieved by reacting ligand **4** with stoichiometric amounts of $Al(NO_3)_3 \cdot 9H_2O$ in ethanol. These compounds were characterized by ^1H NMR, ESI-MS.[10] The mass spectrum of complex **5** exhibited a signal at *m/z* 977.2 corresponding to $[\mathbf{5}+Na]^+$. The experimental result showed that complex **5** had good solubility in most common organic solvent, such as CH_2Cl_2, $CHCl_3$, THF, even in CH_3OH, which showed our aim to prepare soluble Al(III) complex was achieved.

The single crystals of compound **4** were obtained from chloroform/methanol by controlling the concentration of the compound, the crystallization temperature and the velocity of crystallization. The Oak Ridge Thermal Ellipsiod Plot (ORTEP) drawings of the compound are shown in Figure 1. The single crystal adopted a monoclinic space group. The carbazole ring and quinoline ring are almost perpendicular (the dihedral angle between the two rings is 80.57°).[10] The absorption and photoluminescence spectra of complex **5** and Alq_3 were measured in THF (Fig. 2). And the photophysical properties of complex **5** in different solvents are listed in Table 1.

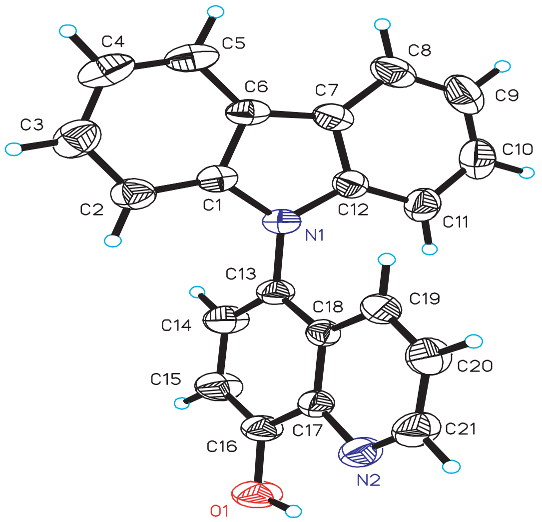

Figure 1. The ORTEP plot of the X-ray crystal structure of compound **4**. Thermal ellipsoids are scaled to the 50% probability level.

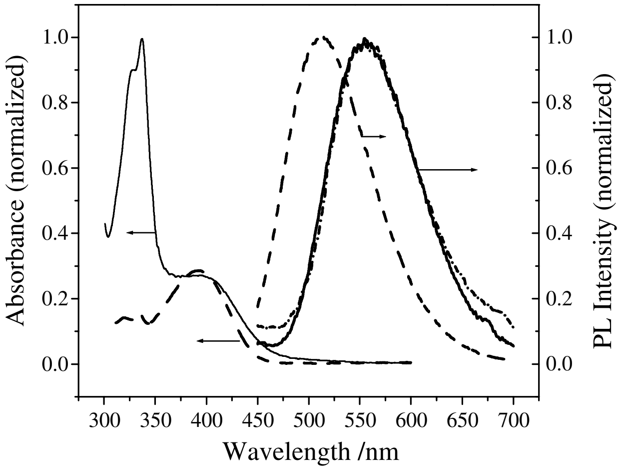

Figure 2. Absorption and emission spectra of Alq_3 (dash line) and compound **5** (solid line) in THF solution and emission spectrum of compound **5** (dash-dot line) in solid powder. Emission spectra recorded on excitation at 399 nm.

Table 1. Photophysical properties of complex **5** in different solvents

Solvents	λ_{abs} (nm)	λ_{em} (nm)	τ_f (ns)[a]
THF	399, 337	554	18.24
CH_3CN	391, 337	557	9.69
CH_3OH	391, 336	558	9.88
CH_2Cl_2	397, 338	558	14.48

[a] Average fluorescence lifetime: $\tau_f = (\alpha_1\tau_1+\alpha_2\tau_2)/(\alpha_1+\alpha_2)$, where α_1 and α_2 are the amplitudes and τ_1 and τ_2 are the lifetimes of two exponential decay function: $\alpha_1 e^{(-t/\tau 1)}+\alpha_2 e^{(-t/\tau 2)}$.

Compared with Alq_3 showing the maximum absorption at 386 nm in THF solution, complex **5** showed intense absorption at 337 nm attributed to the carbazole groups and absorption at 399 nm ascribed to the π–π* transition of the aluminium complex. Additionally, complex **5** emitted at 554 nm whereas Alq_3 did at 514 nm in THF. Because the highest density HOMOs of metalloquinolates are located on the C-5 (*para* position to the oxygen),[7c] electron-donating substituent in the C-5 position would cause a red-shift in the emission and absorption spectra of complex **5**. The PL spectra showed that there existed effective intramolecular singlet energy transfer between carbazole groups and Alq_3 for there was no characteristic PL peak of carbazole even excited at 337 nm. There was a sufficient overlap between the emission of carbazole moiety (peak at 360 nm) and the absorption of the complex, thus singlet–singlet energy transfer from the excited state of carbazole chromophore to Alq_3 ground state would be favourable. And the photoluminescence spectrum of compound **5** in solid powder (shown in Fig. 2) also showed a red-shift, in which compound **5** emitted at 556 nm whereas Alq_3 did at 520 nm. The photoluminescence peaks of compound **5** in solution and solid state were at the same wavelength. In addition, the fluorescent quantum yield of compound **5** was 37% of the fluorescent quantum yield of Alq_3, and the fluorescence lifetime of compound **5** was shorter than that of Alq_3 in the same solution.[11,7m]

The electrochemical property of compound **5** was investigated by cyclic voltammetry at ambient temperature, as shown in Figure 3. In compound **5**, one reversible oxidation redox couple was observed and ascribed to the carbazole unit. The dipolar nature of compound **5** was explained on the cyclic voltammetry involving electron oxidation and electron reduction. Also the dual components of the fluorescent lifetimes (Table 1) of complex **5** in different solvents indicated its dipolar nature.

In this study, the HOMO value was calculated from the oxidation potential versus the internal standard of ferrocene/ferrocenium (Fc) using the semi-empirical method.[12] Complex **5** had two oxidation waves corresponding to mono- and di-radicals. The half oxidation potential of the first oxidation was used to calculate the HOMO energy level, which was -5.51 eV and higher than that of Alq_3 whose HOMO value was -5.90 eV. From this result, we can conclude that the HOMO level of the complex is determined by the carbazole moiety. Thus, the role of the carbazole moiety for significant improvement in the hole transporting can be expected.

In conclusion, a novel soluble Alq_3 derivative was synthesized. The hole-transporter (Carbazole) and electron transporter (Alq_3) were connected directly by Ullmann reaction to obtain a bifunctional and dipolar material. The photophysical, electrochemical properties and applied prospect of the material were investigated.

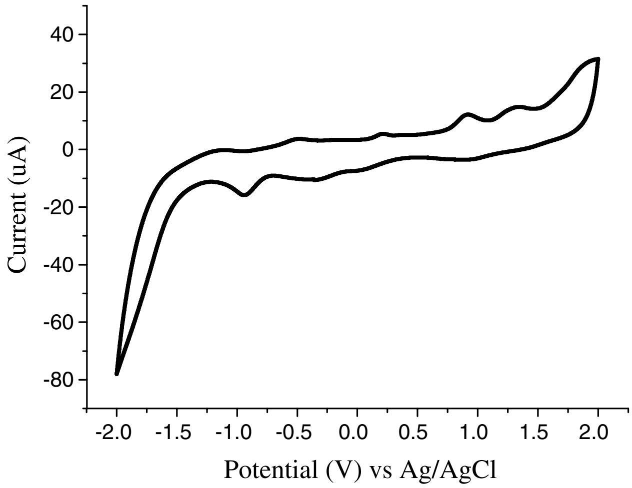

Figure 3. The cyclic voltammogram of complex **5** with 0.1 M *n*-Bu_4NClO_4 in CH_2Cl_2.

Acknowledgements

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References and notes

1. (a) Friend, R. H.; Gymer, R. W.; Holmoes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Logdlund, M.; Salanech, W. R. *Nature* **1999**, *397*, 121–128; (b) Aziz, H.; Popovic, Z.; Hu, X.; Hor, A. M.; Xu, G. *Science* **1999**, *283*, 1900–1902.
2. (a) Song, S. Y.; Jang, M. S.; Shim, H. K.; Hwang, D. H.; Zyung, T. *Macromolecules* **1999**, *32*, 1482–1487; (b) Jiang, X. Z.; Register, R. A.; Killeen, K. A.; Thompson, M. E.; Pschenitzka, F.; Sturm, J. C. *Chem. Mater.* **2000**, *12*, 2542–2579; (c) Tian, H.; Zhu, W. H.; Elschner, A. *Synth. Met.* **2000**, *111*, 481–483; (d) Ng, S. C.; Lu, H. F.; Chan, H. S. O.; Fujii, A.; Laga, T.; Yoshino, K. *Adv. Mater.* **2000**, *12*, 1122–1125; (e) Peng, Z. H.; Pan, Y. C.; Xu, B. B.; Zhang, J. H. *Macromol. Symp.* **2000**, *154*, 245–252; (f) Kwok, C. C.; Wong, M. S. *Macromolecules* **2001**, *34*, 6821–6830; (g) Lee, Y. Z.; Chen, X. W.; Chen, S. A.; Wei, P. K.; Fann, W. S. *J. Am. Chem. Soc.* **2001**, *123*, 2296–2307; (h) Hong, Y. R.; Lee, D. W.; Kim, K.; Jin, J. I.; Lee, C. E.; Lee, H. M.; Park, Y.; Shon, B. H.; Park, J. K. *Macromol. Symp.* **2001**, *175*, 169–176; (i) Zhan, X.; Liu, Y.; Zhu, D.; Jiang, X.; Jen, A. K.-Y. *Macromol. Chem. Phys.* **2001**, *202*, 2341–2345; (j) Liu, Y.; Yu, G.; Li, H.; Tian, H.; Zhu, D. *Thin Solid Films* **2002**, *417*, 107–110.
3. (a) Tamoto, N.; Adachi, C.; Nagai, K. *Chem. Mater.* **1997**, *9*, 1077–1085; (b) Peng, Z. H.; Bao, Z. N.; Galvin, M. E. *Chem. Mater.* **1998**, *10*, 2086–2090; (c) Zhu, W. H.; Tian, H.; Elschner, A. *Chem. Lett.* **1999**, 501–502; (d) Mochizuki, H.; Hasui, T.; Kawamoto, M.; Shiono, T.; Ikeda, T.; Adachi, C.; Taniguchi, Y.; Shirota, Y. *Chem. Commun.* **2000**, 1923–1924.
4. (a) Liu, Y.; Ma, H.; Jen, K.-Y. *Chem. Commun.* **1998**, 2747–2748; (b) Wang, Y. Z.; Epstein, A. J. *Acc. Chem. Res.* **1999**, *32*, 217–224; (c) Jenekhe, S. A.; Lu, L. D.; Alam, M. M. *Macromolecules* **2001**, *34*, 7315–7324.
5. (a) Thomas, K. R. J.; Lin, J.-T.; Tao, Y.-T.; Chuen, C. H. *Chem. Mater.* **2002**, *14*, 3852–3859; (b) Zhang, Y.; Hu, Y.; Li, H.; Wang, L.; Jing, X.; Wang, F.; Ma, D. *J. Mater. Chem.* **2003**, *13*, 773–777; (c) Chen, C.-T.; Lin, J.-S.; Moturu, M. V. R. K.; Lin, Y.-W.; Yi, W.; Tao, Y.-T.; Chien, C.-H. *Chem. Commun.* **2005**, 3980–3982.
6. Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913–915.
7. (a) Curioni, A.; Boero, M.; Andreoni, W. *Chem. Phys. Lett.* **1998**, *294*, 263–271; (b) Curioni, A.; Andreoni, W. *J. Am. Chem. Soc.* **1999**, *121*, 8216–8220; (c) Chen, C. H.; Shi, J. *Coord. Chem. Rev.* **1998**, *171*, 161–174; (d) Wang, S. *Coord. Chem. Rev.* **2001**, *215*, 79–98; (e) Ghedini, M.; Deda, M. L.; Aiello, I.; Grisolia, A. *J. Chem. Soc., Dalton Trans.* **2002**, 3406–3409; (f) Pohl, R.; Anzenbacher, P., Jr. *Org. Lett.* **2003**, *138*, 189–192; (g) Bai, F.; Zheng, M.; Yu, G.; Zhu, D. *Thin Solid Films* **2000**, *363*, 118–121; (h) Wang, G.; Liang, F.; Xie, Z.; Su, G.; Wang, L.; Jing, X.; Wang, F. *Synth. Met.* **2002**, *131*, 1–5; (i) Coelle, M.; Gmeiner, J.; Milius, W.; Hillebrecht, H.; Brutting, W.

Adv. Funct. Mater. **2003**, *13*, 108–112; (j) Xie, J.; Fan, L.; Su, J.; Tian, H. *Dyes Pigments* **2003**, *59*, 153–162; (k) Ma, D.; Wang, G.; Hu, Y.; Zhang, Y.; Wang, L.; Jing, X.; Wang, F.; Lee, C. S.; Lee, S. T. *Appl. Phys. Lett.* **2003**, *82*, 1296–1298; (l) Shen, L.; Li, F.; Sha, Y.; Hong, X.; Huang, C. *Tetrahedron Lett.* **2004**, *45*, 3961–3964; (m) Mishra, A.; Nayak, P. K.; Periasamy, N. *Tetrahedron Lett.* **2004**, *45*, 6265–6268; (n) Pohl, R.; Montes, V. A.; Shinar, J.; Anzenbacher, P., Jr. *J. Org. Chem.* **2004**, *69*, 1723–1725.

8. Lin, B. C.; Cheng, C. P.; You, Z.-Q.; Hsu, C.-P. *J. Am. Chem. Soc.* **2005**, *127*, 66–67.
9. (a) Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1–25; (b) Xia, C.; Advincula, R. C. *Macromolecules* **2001**, *34*, 5854–5859; (c) Koene, B. E.; Loy, D. E.; Thompson, M. E. *Chem. Mater.* **1998**, *10*, 2235–2250; (d) Bach, U.; Cloedt, K. D.; Spreitzer, H.; Cratzel, M. *Adv. Mater.* **2000**, *12*, 1060–1063; (e) Wu, I. Y.; Lin, J. T.; Tao, Y. T.; Balasubramaniam, E. *Adv. Mater.* **2000**, *12*, 668–669; (f) Justin Thomas, K. R.; Lin, J. T.; Tao, Y.-T.; Ko, C.-W. *Adv. Mater.* **2000**, *12*, 1949–1951; (g) Bai, F.; Zheng, M.; Yu, G.; Zhu, D. *Thin Solid Films* **2000**, *363*, 118–121; (h) Justin Thomas, K. R.; Lin, J. T.; Tao, Y.-T.; Ko, C.-W. *J. Am. Chem. Soc.* **2001**, *123*, 9404–9411; (i) Ko, C.-W.; Tao, Y.-T.; Lin, J. T.; Justin Thomas, K. R. *Chem. Mater.* **2002**, *14*, 357–361; (j) Justin Thomas, K. R.; Lin, J. T.; Tao, Y.-T.; Ko, C.-W. *Chem. Mater.* **2002**, *14*, 1354–1361; (k) Strohriegl, P.; Grazulevicius, J. V. *Adv. Mater.* **2002**, *14*, 1439–1452; (l) Zhang, L. Z.; Chen, C. W.; Lee, C. F.; Wu, C. C.; Luh, T. Y. *Chem. Commun.* **2002**, 2336–2337; (m) Zhang, Q.; Chen, J.; Cheng, Y.; Wang, L.; Ma, D.; Jing, X.; Wang, F. *J. Mater. Chem.* **2004**, *14*, 895–900.
10. Selected characterization data of the intermediates, ligand and complex. Compound **2**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.91(d, 1H, $J = 1.55$), 8.36 (d, 1H, $J = 6.95$), 8.03 (d, 1H, $J = 3.97$), 7.53 (d, 1H, $J = 4.37$), 6.86 (d, 1H, $J = 7.28$), 4.09 (s, 3H, OCH$_3$); ESI-MS *m/z* 236.8, 238.8. Compound **3**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.99 (d, 1H, hydroxyquinoline, $J = 2.54$), 8.21 (d, 2H, carbazole, $J = 7.69$), 7.66 (d, 1H, hydroxyqinoline, $J = 8.17$), 7.52 (d, 1H, hydroxyquinoline, $J = 7.02$), 7.37–7.23 (m, 6H, carbazole and hydroxyqinoline), 6.97 (d, 2H, carbazole, $J = 7.96$), 4.23 (s, 3H, OCH$_3$); ESI-MS *m/z* (M)$^+$: 324.13. Ligand **4**: ^{1}H NMR (500 MHz, d_6-DMSO) δ 10.45 (b, 1H, OH), 8.92 (d, 2H, hydroxyquinoline, $J = 2.97$), 8.29 (d, 2H, carbazole, $J = 7.72$), 7.69 (d, 1H, hydroxyquinoline, $J = 8.07$), 7.44 (d, 1H, hydroxyqinoline, $J = 4.49$), 7.36–7.26 (m, 6H, carbazole and hydroxyquinoline), 6.92 (d, 2H, carbazole, $J = 8.05$); ESI-MS *m/z* (M)$^+$: 310.11. Compound **5**: ESI-MS *m/z* (M+Na)$^+$: 977.2.
    Crystallographic data (excluding structure factors) for the structure in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 282458. Copies of the data may be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 (0) −1223– 336033 or email: deposit@ccdc.cam.ac.uk). Crystal data: Green plates, C$_{21}$H$_{14}$N$_2$O, $FW = 310.34$, $T = 293$ (2) K, monoclinic, space group$P2(1)/n$, $a = 8.2571$ (7) Å, $\alpha = 90°$, $b = 7.9154$ (7) Å, $\beta = 97.538$ (2)°, $c = 24.900$ (2) Å, $\gamma = 90°$, $V = 1613.3$ (2) Å^3, $\rho_{(\mathrm{calcd})} = 1.278$ Mg/m^3, $\mu = 0.080$ mm^{-1}, $Z = 4$, reflections collected: 9189, independent reflections: 3493 ($R_{\mathrm{init}} = 0.0634$), final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0469$, w$R_2 = 0.1245$; R indices (all data): $R_1 = 0.0599$, w$R_2 = 0.1313$.
11. Absolute fluorescence quantum yield of Alq$_3$ in dichloromethane is 0.22: Ravi Kishore, V. V. N.; Narasimhan, K. L.; Periasamy, N. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1386–1391.
12. (a) Pommerehne, J.; Vestweber, H.; Giss, W.; Mahrt, R. F.; Bassler, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551–554; (b) He, M.; Twieg, R. J.; Gubler, U.; Wright, D.; Moerner, W. E. *Chem. Mater.* **2003**, *15*, 1156–1164.