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Efficient blue emission from siloles

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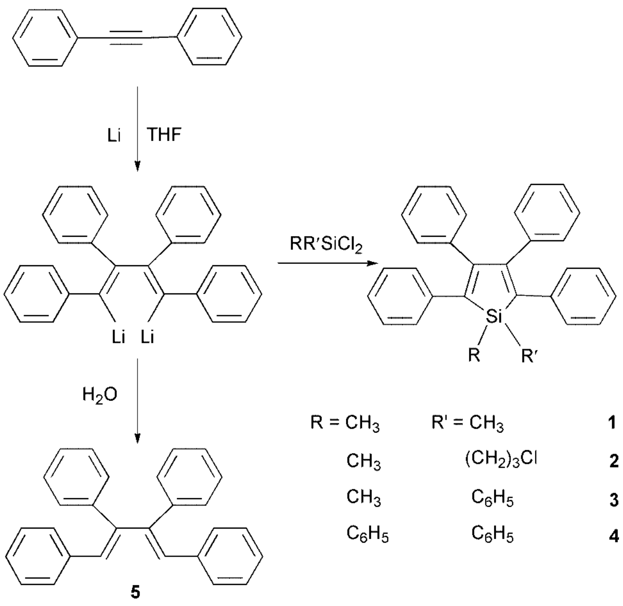
2,3,4,5-Tetraphenylsiloles with different 1,1-substituents on the ring silicon atoms, *i.e.*, 1,1-dimethyl-2,3,4,5-tetraphenylsilole (**1**), 1-methyl-1-(3-chloropropyl)-2,3,4,5-tetraphenylsilole (**2**), 1-methyl-1,2,3,4,5-pentaphenylsilole (**3**) and hexaphenylsilole (**4**), are synthesized and characterized. While all the siloles emit intense blue light readily observable by naked eyes under normal room illumination conditions, the film of their acyclic cousin without silicon, namely 1,2,3,4-tetraphenylbutadiene (**5**), does not fluoresce, revealing the vital role of the planar and rigid silacyclopentadiene ring in the solid-state photoluminescence process. The electronic transitions of the siloles can be tuned by varying the 1,1-substituents, and the inductive and conjugating effects of the aromatic rings confer low LUMO energy levels and high emission efficiencies on the phenyl-substituted siloles. The electroluminescence device of the 1-phenylsilole **3** shows a high brightness (4538 cd m^{-2} at 18 V) and an excellent external quantum efficiency (0.65% at 17 V and 94 mA cm^{-2}).

Introduction

Efficient red, green and blue electroluminescent emitters are indispensable for the design and construction of high quality full-color display devices.[1] Although red and green organic light-emitting diodes (LEDs) have already achieved high brightness and efficiency, strong blue emitters are still rare. Recently, some organometallic complexes containing boron, aluminium, beryllium and zinc atoms have attracted scientists' attention as blue-emitting materials due to their high luminescence efficiency, easy isolation and purification and high quality of color of the emitted light.[2–5]

Silicon is a metalloid element and bears both nonmetallic and metallic characteristics. Organosilicon compounds are in general much more stable than their cousins of aluminium, beryllium and zinc complexes. Siloles or silacyclopentadienes are a group of Si-containing conjugated rings with novel molecular structures and unique electronic properties.[6] Siloles possess low-lying LUMO energy levels associated with the σ^*–π^* conjugation arising from the interaction between the σ^* orbital of two exocyclic σ-bonds on the ring silicon and the π^* orbital of the butadiene moiety.[7] As a result, siloles can serve as efficient electron-transport materials in LED devices.[8] Silole polymers have been found to show interesting photo- (PL) and electroluminescence (EL) properties;[8,9] for example, an EL device based on a silole-containing polysilane, poly(2′,3′,4′,5′-tetraphenyl-1′-silacyclopenta-2′,4′-diene-1′,1′-diyl-1,1,2,2,3,3,4,4-octamethyltetrasilanylene), emitted blue light of 488 nm with a maximum external quantum efficiency of 0.001% and a maximum luminance of 5 cd m^{-2} at 22 V.[8]

Silole is rich in chemistry and a wide variety of silole derivatives can be readily prepared by "simple" chemical reactions.[6,10] Systematic investigation on the luminescence properties of the silole derivatives have, however, not been performed. During our search for highly luminescent materials,[11] we were attracted by the structural feature of silole, which resembles fluorene in terms of ring planarity and rigidity but offers more possibilities in structural modification and hence property modulation. In this work, we took a molecular engineering approach and systematically synthesized a series of siloles with different 1,1-substituents on the ring silicon atoms (**1**–**4**, Scheme 1). All the siloles are stable in air (and hence easily to handle) and can be readily fabricated into EL devices by conventional vapor deposition techniques. Similar to the silole polymer[8] discussed above, the EL devices of the siloles **1**–**4** also emit blue light (λ_{max} ~490 nm). The luminance and external quantum efficiency of the 1-phenylsilole **3** are, however, 2–3 orders of magnitude higher than those of the silole polymer.[8]



Scheme 1 Synthetic route to compounds **1–5**.

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Experimental

Materials

High-purity lithium (Acros), diphenylacetylene, dichloro(dimethyl)silane, dichloro(3-chloropropyl)methylsilane, dichloro(diphenyl)silane and dichloro(methyl)phenylsilane (all from Aldrich) were used as received without further purification. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl under nitrogen prior to use.

Instrumentation

Melting points were determined on a Yanaco MP-500 melting point apparatus. FT-IR spectra were recorded on a Perkin–Elmer System 2000 spectrophotometer using KBr pellets. Electronic absorption spectra were taken in dilute chloroform solutions (~0.05 mM) on a General TU-1201 UV-vis spectrophotometer. ^{1}H NMR spectra were obtained in chloroform-*d* on a Bruker ARX300 NMR spectrometer and the spectral data are expressed in δ scale relative to the internal standard of tetramethylsilane. Mass spectra were measured on AEI-MS50 using electron impact (EI) mode. Elemental analyses were carried out on a Carlo Erba Model 1106 elemental analyzer.

Synthesis

The synthesis of compounds **1** and **3–5** was reported in the literature,[12] but all these compounds were not fully characterized, and only UV and/or IR data were given. Here, we report the simple one-pot synthesis of these compounds and present the full characterization data including elemental analysis, IR, ^{1}H NMR and MS. Compounds **1–5** were prepared by treating diphenylacetylene with lithium followed by hydrolysis or reaction with dichlorosilicons as shown in Scheme 1.

1,1-Dimethyl-2,3,4,5-tetraphenylsilole (1). To a solution of diphenylacetylene (4.5 g, 25 mmol) in dry THF (20 mL) was added clean lithium shavings (350 mg, 50 mmol). The reaction mixture was stirred at room temperature for 2 h in a dry nitrogen atmosphere. The mixture was then diluted with 120 mL of THF, followed by the addition of 1.6 g (12.5 mmol) dichloro(dimethyl)silane. After refluxing for 5 h, the reaction mixture was cooled and filtered and the filtrate was washed with water. The organic layer was extracted with diethyl ether and dried over magnesium sulfate. The solvent was removed and the residue was purified by flash chromatography over silica gel using 10% diethyl ether in petroleum ether as eluent. Recrystallization from ethanol gave a faintly greenish–yellow crystal in 70% yield (3.6 g). Mp = 177–178 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12 (m, 6H), 7.01 (m, 6H), 6.96 (m, 4H), 6.84 (m, 4H), 0.49 (s, 6H). FT-IR (KBr): 3077, 3058, 3023, 2956, 1595, 1488, 1441, 1297, 1245, 1089, 1075, 1029, 938, 913, 836, 795, 777, 743, 709, 697, 579 cm^{-1}. MS (EI): *m*/*z* 414 (calcd for $C_{30}H_{26}Si$ 414.62). Anal. Calcd for $C_{30}H_{26}Si$: C, 86.91; H, 6.32. Found: C, 86.50; H, 6.42%.

1-Methyl-1-(3-chloropropyl)-2,3,4,5-tetraphenylsilole (2). This compound was prepared by a procedure similar to that of **1**, using dichloro(3-chloropropyl)methylsilane instead of dichloro(dimethyl)silane; the product was isolated as a faintly greenish–yellow crystalline solid in 74% yield (4.4 g). Mp = 94–95 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.13 (m, 6H), 7.01 (m, 6H), 6.93 (m, 4H), 6.81 (m, 4H), 3.48 (t, 2H, *J* 6.7), 1.84 (m, 2H), 1.14 (m, 2H), 0.51 (s, 3H). FT-IR (KBr): 3056, 3024, 2954, 1596, 1573, 1489, 1441, 1298, 1252, 1089, 1075, 1027, 1003, 937, 915, 806, 790, 762, 711, 697, 578, 483 cm^{-1}. MS (EI): *m*/*z* 477 (calcd for $C_{32}H_{29}SiCl$ 477.12). Anal. Calcd for $C_{32}H_{29}SiCl$: C, 80.56; H, 6.13. Found: C, 80.62; H, 6.12%.

1-Methyl-1,2,3,4,5-pentaphenylsilole (3). This compound was prepared by a procedure similar to that of **1**, using dichloro(methyl)phenylsilane instead of dichloro(dimethyl)silane; the product was isolated as a faintly greenish–yellow crystalline solid in 78% yield (4.6 g). Mp = 170–171 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (m, 2H), 7.39 (m, 3H), 7.04 (m, 12H), 6.88 (m, 8H), 0.81 (s, 3H). FT-IR (KBr): 3055, 3023, 1596, 1488, 1441, 1429, 1298, 1267, 1251, 1110, 1088, 1074, 1027, 937, 913, 798, 762, 738, 726, 710, 697, 498, 474 cm^{-1}. MS (EI): *m*/*z* 476 (calcd for $C_{35}H_{28}Si$ 476.69). Anal. Calcd for $C_{35}H_{28}Si$: C, 88.19; H, 5.92. Found: C, 88.19; H, 6.06%.

Hexaphenylsilole (4). This compound was prepared by a procedure similar to that of **1**, using dichloro(diphenyl)silane instead of dichloro(dimethyl)silane; the product was isolated as a faintly greenish–yellow crystalline solid in 68% yield (4.6 g). Mp = 186–187 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (m, 4H), 7.43 (m, 6H), 7.20–6.85 (m, 20H). FT-IR (KBr): 3055, 3024, 1597, 1485, 1441, 1429, 1298, 1111, 1074, 1027, 790, 764, 741, 713, 697, 509 cm^{-1}. MS (EI): *m*/*z* 538 (calcd for $C_{40}H_{30}Si$ 538.76). Anal. Calcd for $C_{40}H_{30}Si$: C, 89.18; H, 5.61. Found: C, 89.46; H, 5.56%.

1,2,3,4-Tetraphenylbutadiene (5). To a solution of diphenylacetylene (1.8 g, 10 mmol) in dry THF (5 mL) was added clean lithium shavings (140 mg, 20 mmol). The reaction mixture was stirred at room temperature for 2 h under nitrogen. The unreacted lithium was filtered off and the filtrate was washed with water. The organic layer was extracted with diethyl ether and dried over magnesium sulfate. The solvent was removed and the residue was purified by flash chromatography over silica gel using *n*-hexane as eluent. Recrystallization from ethanol gave a pale yellow crystal in 75% yield (1.35 g). Mp = 183–184 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41–7.30 (m, 10H), 7.02 (m, 6H), 6.74 (m, 4H), 6.30 (s, 2H). FT-IR (KBr): 3081, 3060, 3026, 1634, 1596, 1489, 1443, 1357, 1073, 1027, 917, 870, 786, 762, 752, 704, 692, 574, 549, 477 cm^{-1}. MS (EI): *m*/*z* 358 (calcd for $C_{28}H_{22}$ 358.48). Anal. Calcd for $C_{28}H_{22}$: C, 93.81; H, 6.19. Found: C, 93.96; H, 6.11%.

LED fabrication and luminescence measurements

Thin films of **1–5** were deposited on quartz substrates by vapor vacuum deposition technique, whose PL spectra were recorded on a Hitachi F-4500 spectrofluorometer using 360 nm as the excitation wavelength. Substrates used were indium–tin oxide (ITO) glass with a sheet resistance of 100 Ω square^{-1}. The ITO-coated glass substrates were etched, patterned, and washed with water, acetone and isopropyl alcohol sequentially. The EL devices using the siloles as the emitting layers were fabricated on the ITO substrates. *N*,*N*′-Diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD) and tris(8-hydroxyquinoline)-aluminium (Alq_3) were used as the hole- and electron-transport layers, respectively. The TPD (~50 nm), silole (~50 nm) and Alq_3 (~30 nm) layers and aluminium cathode were deposited onto the ITO substrate by vacuum evaporation at pressure close to 10^{-6} Torr. The deposition rate for the organic layers was about 2 Å s^{-1}. Luminance was measured with an LS-1 portable luminometer. Current–voltage characteristics for the LEDs with a structure of ITO/TPD(50 nm)/silole(50 nm)/Alq_3(30 nm)/Al were measured with a PA meter/DC voltage source (HP4140B). All the measurements were performed in ambient atmosphere at room temperature.

Results and discussion

Electronic absorption

UV absorption spectra of the chloroform solutions of **1–5** are shown in Fig. 1A. All the siloles **1–4** exhibit two peaks at ~250

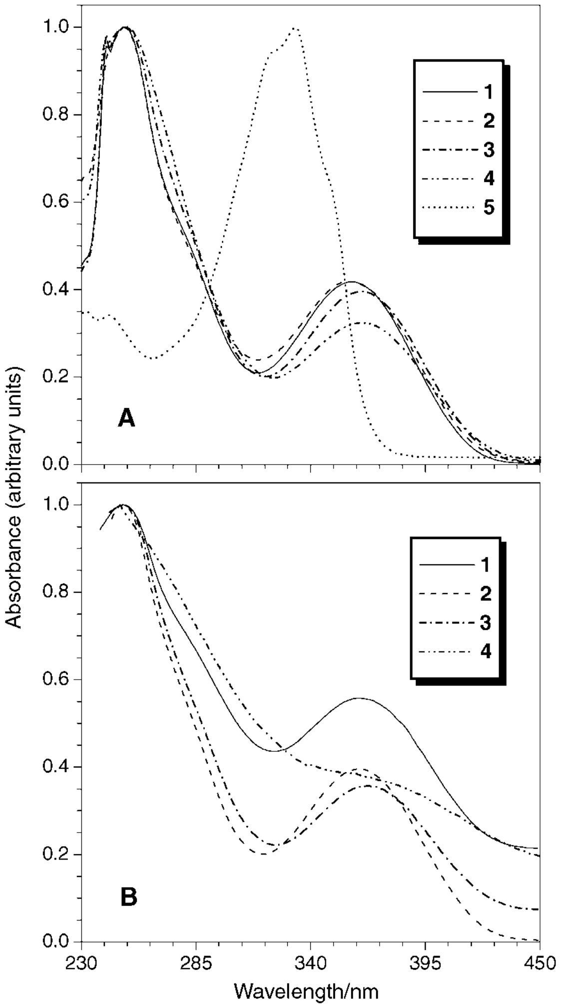

Fig. 1 Absorption spectra of (A) chloroform solutions of **1–5** and (B) thin films of **1–4**.

and ~360 nm; the former is attributed to the π–π* transition of the phenyl groups and the latter is due to the π–π* transition of the silacyclopentadiene ring. The band gaps (E_g) of the siloles are estimated from the onset positions of the absorption bands[11] to be 2.97, 2.97, 2.93 and 2.90 eV, respectively, while the E_g of **5** is 3.35 eV. The large difference between the band gaps of the siloles and their acyclic cousin **5** clearly demonstrates the significant structural and electronic effects of the ring silicon atom on the electronic transition of the π-conjugated system. The fixation of the labile *cis*-cisoid butadiene structure by the silicon atom gives a fluorene-like planar and rigid ring structure[9] and the unique orbital interactions such as σ*–π* conjugation lower the LUMO energy levels;[9] the synergistic interplay of the two effects leads to the observed low E_g of the siloles.

The 1,1-substituents on the silicon atom affect the absorption spectra of the siloles in a unique way. Replacing one of the two 1,1-dimethyl groups in **1** with a 3-chloropropyl group brings about little change to the absorption peak in the long wavelength region; the λ_{max} of **2** being practically identical to that of **1**. This may be understood by the fact that methyl and propyl both belong to the same category of electron-donating alkyl groups. Substitution of the methyl group by a phenyl group (**3**), however, red-shifts the absorption spectrum. Further red-shift is induced when the two methyl groups in **1** are replaced by two phenyl rings in **4**. Clearly the electron-withdrawing phenyl groups exert a bathochromic effect on the electronic transitions of the siloles. In other words, the electronic structures and properties of the siloles can be readily tuned by molecular engineering of the inductive effects of the 1,1-substituents.

Tamao and coworkers have investigated the substituent effects in an analoguous system, *i.e.*, 3,4-dimethyl-2,5-bis(trimethylsilyl)siloles, and found that the inductive effect plays a major role in modifying the electronic structures of the siloles.[13] Our observation in the 2,3,4,5-tetraphenylsilole system is thus consistent with Tamao's early finding. Theoretical calculations reveal that the phenyl group does not only lower the LUMO energy level but also slightly raises the HOMO energy level of a silole,[13] suggesting that the extended σ*–π* conjugation over the phenyl ring on the silicon atom may also play a role in red-shifting the absorption spectrum of a silole. Fig. 1B shows the absorption spectra of the thin solid films of the siloles, which are similar to those measured in the solutions. Thus the electronic transitions of the siloles are primarily determined by their molecular structures, which are insignificantly affected by their aggregation states.

Photoluminescence

The great similarity between PL and EL spectra of many light-emitting materials suggests that similar mechanisms are at play or that the same emitting species (a singlet exciton) is involved in each case.[14] Because of the simplicity of the PL measurements, we first checked the PL behaviors of the siloles **1–4** and their structural cousin **5**. Fig. 2 shows the PL spectra of the thin solid films of the siloles. All the siloles emit strong blue light upon photoexcitation. Compared to those of the siloles with 1,1-dialkyl substituents (**1** and **2**), the PL spectra of the siloles with phenyl substituents on the ring silicon atoms (**3** and **4**) are located in the longer wavelength region. Thus the phenyl rings induce red-shifts in the PL spectra of the siloles, probably again due to the inductive and σ*–π* conjugating effects of the aromatic rings.

The thin film of the acyclic carbon analog of the siloles (**5**), however, emits hardly observable PL signals. The rotation of the unfixed cisoid structure of **5** in three-dimensional space may unfavorably perturb the electronic structure, giving a non-planar structure with inefficient π-conjugation. The fixation of the *cis*-cisoid butadiene moiety in the siloles by the silicon atom creates a polar and rigid ring structure. It is well known that increasing planarity and rigidity helps to increase fluorescence efficiency as it enhances the free mobility of the π electrons and charge transportation.[14] Increased rigidity can also help by reducing vibrational–rotational interactions in the excited state that can lead to intersystem crossing. Fluorene ring and acyclic biphenyl are the "classic" examples in this regard, with the former possessing a much higher quantum efficiency than the

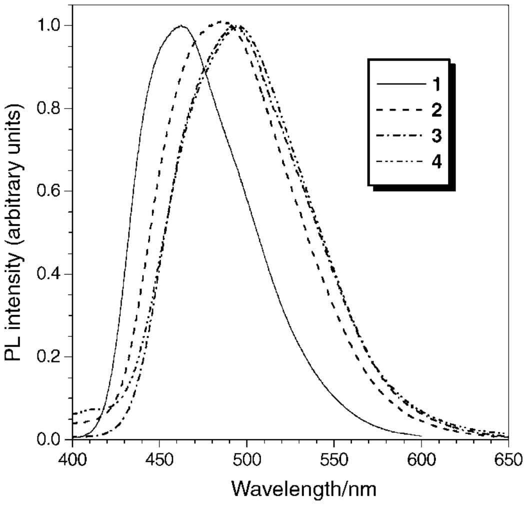

Fig. 2 Photoluminescence spectra of thin solid films of siloles **1–4**.

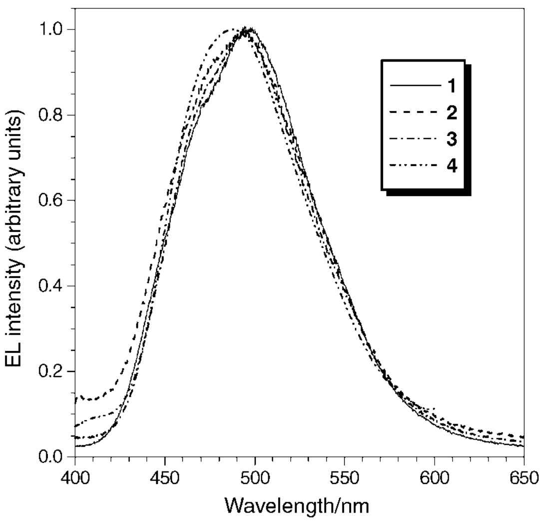

Fig. 3 Electroluminescence spectra of the ITO/TPD/silole/Alq_3/Al devices.

latter.[15] The difference in the PL properties of the silole rings and their acyclic cousin **5** is even more dramatic and striking, presenting an excellent example demonstrating the importance of molecular planarity and rigidity in the photophysical process.

Electroluminescence

The efficient PL emission from the siloles prompted us to check their EL behaviors, whereas **5** was not further studied because of its PL inactivity. The EL devices were fabricated using the silole, TPD and Alq_3 as the light-emitting, hole-transport and electron-transport layers, respectively. Fig. 3 shows the EL spectra of the siloles, which are similar to their PL spectra with the emission maximums located at ~490 nm. This suggests that the blue emission comes mainly from the radiative decay of the singlet excitons of the siloles formed by the recombination of holes and electrons injected from the TPD and Alq_3 layers, respectively.

The current–voltage–brightness curves of the EL device of a silole, that is **3**, are given in Fig. 4. The device shows an excellent diode behavior: under the forward bias (a positive voltage applied to the ITO electrode), the current increases exponentially with an increase in the applied voltage after exceeding the turn-on voltage. In contrast, under reverse bias, no obvious increase in the current density is observed when the applied voltage is increased. The device has a turn-on voltage of 11 V, a high brightness of 139 μW (corresponding to a luminance of 4538 cd m^{-2}) at 18 V, and an excellent external quantum efficiency of 0.65% at 17 V and 94 mA cm^{-2}. This is one of the best results for blue EL devices using aluminium as the cathode.[14,16,17]

Table 1 Performance of the EL devices of the siloles[a]

Silole	Turn-on voltage/V	Emission maximum/nm	Brightness[b]/ μW	External quantum efficiency[c] (%)
1	9	494	6.8	0.026
2	7	494	0.7	0.0045
3	11	494	138.7	0.65
4	12	488	36.3	0.31

[a] Configuration of the devices: ITO/TPD/silole/Alq_3/Al. [b] At 14 (**1**), 12 (**2**), 18 (**3**) and 21 V (**4**). [c] At 141 (**1**), 7.14 (**2**), 94 (**3**) and 1.9 mA cm^{-2} (**4**).

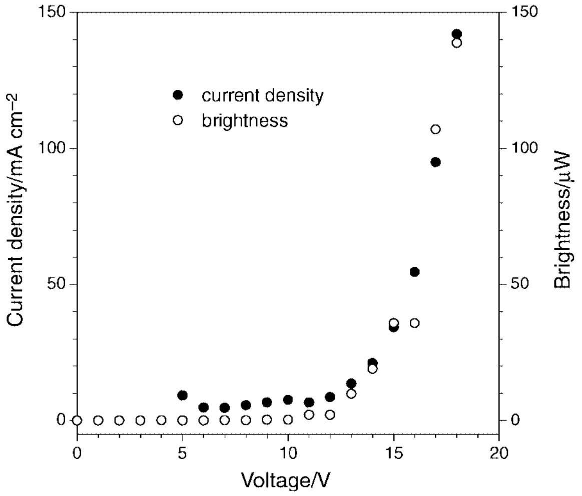

Fig. 4 Current–voltage–brightness characteristics of ITO/TPD/**3**/Alq_3/Al device.

The EL data of the silole devices are summarized in Table 1. All the devices emit blue light of ~490 nm. The substituents on the ring silicon atoms largely affect the EL properties of the siloles. The siloles with electron-withdrawing and σ^*–π^* conjugating 1,1-(di)phenyl group(s) (**3** and **4**) show much higher brightness and external quantum efficiencies than their counterparts with alkyl groups (**1** and **2**). Moreover, the high melting points of **3** and **4** should be emphasized as a very important attribute to prevent crystallization that leads to device failure. While the device performance of **2** is only slightly better than that of Adachi's silole polymer,[8] the 1-phenylsilole **3** greatly outperforms the 1,1-dialkylsilole **2**—it is truly remarkable that the EL properties of the siloles can be manipulated to such a great extent (2 orders of magnitude) by simply varying the type of the 1-substituent.

Conclusions

Four siloles are synthesized by a simple chemical reaction in a one-pot procedure. The structural planarity and rigidity endow the siloles with excellent luminescencent properties, which can be further tuned by varying the 1,1-substituents on the ring silicon atoms. The EL device of the 1-phenylsilole **3** emits blue light with a high brightness and an excellent external quantum efficiency. Noting that a figure of 100 cd m^{-2} is considered bright enough for a flat panel display,[16,17] the extremely high luminance of **3** (4538 cd m^{-2}) makes the silole a promising candidate for luminescent materials to be used in LED devices and systems.

Acknowledgements

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