Making silole photovoltaically active by attaching carbazolyl donor groups to the silolyl acceptor core†

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Appending carbazolyl groups to a hexaphenylsilole core yielded thermally and morphologically stable carbazolylsiloles; the silole carrying two carbazolyl peripheral groups showed photovoltaic activity.

Siloles are a group of wonder molecules that exhibit an array of unusual properties.¹ For example, siloles virtually do not emit when isolated in dilute solutions but emit intensely when aggregated in the solid state, a novel phenomenon for which we coined the term aggregation-induced emission (AIE).²,³ The spectral widths and emission colours of their solid films are narrower and bluer, respectively, than those of their dilute solutions.⁴ Furthermore, photoluminescence (PL) spectra of their crystals blue-shift from those of their amorphous films.⁵,⁶ All of these behaviours are opposite to those of “normal” luminophors. Utilizing these unique properties, we developed silole-based visco-, thermo-⁷ and vapochromic systems⁸ and constructed silole-based chemo- and biosensors for detecting chemical (e.g., explosives)⁹ and biological analytes (e.g., antibodies).⁰ We fabricate silole-based light-emitting diodes (LEDs), which emit brilliantly (luminance up to 55880 cd/m²) and efficiently (external quantum efficiency up to 8%).¹²,¹³

Fast electron mobilities have been reported for thin solid films of siloles,⁴,¹⁰ and many groups have used siloles as electron transport materials in the construction of electroluminescence (EL) devices.¹¹ This fact spurred our interest in using siloles as active materials to construct photovoltaic (PV) cells. Our initial attempts, however, ended with dismay: none of the siloles we tested gave meaningful PV signals. It has been well recognized that excitons dissociate efficiently at a donor (D)–acceptor (A) heterojunction interface.¹²–¹⁴ Siloles are excellent electron acceptors, because their LUMO levels are lowered by their unique σ*–π* conjugations.¹,³,¹¹,¹⁵ Carbazole (Cz), on the other hand, is a well-known electron donor and widely used hole transport material. We envisage that introduction of Cz donor groups into the silole acceptor system may create photo-responsive D–A adducts. In this work, we attached Cz group(s) to the 1-position of hexaphenylsilole (HPS; Fig. 1). Whereas the HPS derivative with one Cz group (CzHPS) did not work well as a PV material, its congener with two Cz groups (C2zHPS) exhibited high PV activity.

The Cz moieties are incorporated into the silole structure by desalt coupling: reactions of 1-chloropentaphenylsilole (1) and 1,1-dichlorotetraphenylsilole (2) with 9-(p-lithiobenzyl)carbazole (3) yield the HPS derivatives CzHPS and Cz2HPS, respectively (Fig. 1), which are thoroughly purified and fully characterized (see ESI for details). While we failed to get a crystal of Cz2HPS, a single crystal of CzHPS was grown from a chloroform/acetonitrile mixture, whose crystallographic analysis duly confirmed the structure derived from its spectroscopic data.†

Thermal stability is an important criterion for evaluating the candidacy of a molecule for optoelectronic applications because of the involvement of thermal processes in the device fabrications and operations. The molecule, for example, needs to be sublimed at high temperatures in the vapour deposition process and experiences repeated annealing by the heat generated when the device is put in use. We investigated the thermal behaviours of the new carbazolyl-siloles using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA analyses reveal that CzHPS and Cz2HPS lose 5% of their original weights at 360.4 and

† Electronic supplementary information (ESI) available: preparation and characterization details for CzHPS and Cz2HPS, crystallographic data for CzHPS, and fabrication procedures for the LED devices and PV cells. See http://www.rsc.org/suppdata/cc/b5/b505683g/index.sht

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Fig. 1 Synthesis of Cz2HPS’s and crystal structure of CzHPS. Molecular structure of their parent form of HPS is given in the inset for reference.
347.6 °C, respectively, while their HPS parent does so at 282.4 °C (Fig. 2). Clearly, the introduction of the Cz groups helps enhance the silole’s thermal stability.

The Cz groups also help increase HPS’s glass (\(T_g\)) and melting transition temperatures (\(T_m\)). While \(T_g\) of HPS is 62.4 °C, those of CzHPS and Cz2HPS are much higher, being 95.3 and 129.3 °C, respectively. Similarly, HPS starts its melting transition from 182 °C, but CzHPS and Cz2HPS do so at 234 and 298 °C, respectively. Several crystallization transitions are recorded in HPS during the DSC heating scan. These transitions occur in the CzHPS system at higher temperatures, but no such transitions are detectable in the Cz2HPS system. Cz2HPS thus enjoys strong thermolytic resistance and high morphological stability.

After studying the thermal transitions of the siloles, we checked their electronic transitions. As shown in Fig. 3A, a CzHPS solution in acetone exhibits two UV peaks at 331 and 345 nm, which are assignable to the absorptions by the Cz and silolyl chromophores, respectively, by comparison with the absorption spectra of Cz16 and HPS.3 When a large amount (92 vol%) of water, a non-solvent of CzHPS, is added into the acetone solution, the CzHPS molecules aggregate into nanodimensional clusters, as evidenced by the visual transparency of the resultant suspension. The UV spectrum of the nanoaggregates is slightly red-shifted from that of their isolated species in the dilute solution. A similar phenomenon is observed in the Cz2HPS system.

The solutions of Cz2HPS’s in acetone display weak PL spectra peaked at 366 nm, with very small bumps at ~ 498 nm (Fig. 3B). 9-Methylcarbazole emits strongly at ~ 364 nm with a quantum yield (\(\eta_{PL}\)) of 51%.16 The weak emissions of the Cz groups of Cz2HPS’s at 366 nm are indicative of intramolecular energy transfer in the dilute solutions: the light emitted from the Cz groups is partially absorbed by the HPS core. The molecularly dissolved HPS species are almost nonemissive,30 hence the barely recognizable bumps at ~ 498 nm.

Upon addition of a large amount (92%) of water into the silole solutions, the Cz2HPS molecules cluster into nanoaggregates. The silole emissions at ~ 497 nm become much stronger, revealing that Cz2HPS’s, like their HPS parent, are also AIE-active.2,3 The \(\eta_{PL}\) of the aggregates of CzHPS (56%) is ~ 2.4-fold higher than that of Cz2HPS (23%). This suggests that part of the excited singlet state of Cz2HPS has been quenched through charge dissociation, which is understandable, because the formation of D–A complexes should be a more favorable process in the aggregates of the HPS derivative carrying more Cz units.

We fabricated LEDs using Cz2HPS’s as the host emitters. The EL spectra of the devices (Fig. 3C) resemble the PL spectra of their nanoaggregates in the acetone/water mixture, confirming that the EL and PL originate from the same species of Cz2HPS molecules. The EL characteristics of an LED of CzHPS (device I)17 are shown in Fig. 4A as an example. The device is turned on at ~ 5 V and emits with a maximum current efficiency (\(\eta_c\)) of 2.6 cd/A at 8.5 V. The \(\eta_c\) (2.2 cd/A) of the LED of Cz2HPS (device II)17 is lower than that of CzHPS, in agreement with the trend observed for their \(\eta_{PL}\). More excitons may have been annihilated by more efficient charge dissociation in the Cz2HPS device, because of its...
higher statistic probability of forming D–A interfaces. This is verified by the result of device III:18 its ηe is as low as merely 0.018 cd/A.

Efficient charge dissociation at the D–A heterojunction interface is bad for LED but good for PV application and Cz2HPS may hence show good PV performance. Under the influence of an applied bias, the dissociated holes and electrons in the respective D and A domains may steadily migrate along the interfaces to corresponding electrodes to finish the PV process of converting light to electricity. We examined the PV responses of the CzHPS- and Cz2HPS-based devices (I and II) by shining on them a UV light (365 nm) of low power (15 mW/cm²) under applied biases and found their external quantum efficiencies (ηpv) to be 0.14% and 0.27%, respectively. This confirms that Cz2HPS is a better PV material than CzHPS.

This conclusion is substantiated by the performance of a series of PV cells of Cz2HPS. As can be seen from Fig. 4B, all of the PV cells of Cz2HPS (devices III–VIII) show good PV efficiencies. The best results are obtained with device V, whose short-circuit current is 13.99 mA, open-circuit voltage is 0.21 V, and fill factor is 72%. Although the structure of the cell is far from ideal, we anticipate that an HPS derivative with its silole core fully covered with two Cz groups, and Cz2HPS-based devices (I and II) by shining on them a UV light (365 nm) of low power (15 mW/cm²) under applied biases and found their external quantum efficiencies (ηpv) to be 0.14% and 0.27%, respectively. This confirms that Cz2HPS is a better PV material than CzHPS.

In summary, in this work, we synthesized Cz2HPS’s comprised of carbazolyl donors and silole acceptors. The HPS derivative with two Cz groups, i.e. Cz2HPS, is thermally resistant (Tg 360 °C) and morphologically stable (Tg 129 °C, Tm 298 °C), thanks to the strong D–A interaction in the carbazolylsilole. We have proved the concept that a silole can be made PV-active by attaching donor groups to the silole ring. The PV cells of Cz2HPS perform well and offer an ηpv as high as 2.19%. Optimization of the device structure may further boost the ηpv of the Cz2HPS-based PV cell.

In conclusion, this work is a significant contribution to the field of organic photovoltaics. The Cz2HPS-based devices show promising performance, and further improvements are expected with optimized device structures. The results presented in this work open up new possibilities for the development of efficient and stable organic solar cells.