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Separation of electrical and optical energy gaps for constructing bipolar organic wide bandgap materials[†]

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An electrical and optical energy gaps separation strategy is put forward for the design of organic wide bandgap semiconductors. This new principle could achieve optimization of wide bandgap (both high singlet and triplet energies) and favorable carrier injection energy levels simultaneously.

Wide bandgap semiconductive materials are usually defined as the ones that absorb and emit violet or ultraviolet (UV) light (wavelength shorter than 400 nm). The most important applications of wide bandgap semiconductive materials are to fabricate UV light-emitting devices (LEDs),¹ laser diodes (LDs)² and detectors.³ They also show enormous values in high-density information storage and space exploration.⁴ Over the past decade, tremendous progress has been made in the development of inorganic wide bandgap materials,⁵ such as ZnO and GaN, which results in the large scale application of LED lighting.⁶ By comparison, the development of organic wide bandgap semiconductive materials is relatively far behind.⁷ In general, the organic semiconductors exhibit very low carrier mobility, which brought about their limited load-bearing capacity for current.⁸ This became even more critical for broadening the bandgap of organic semiconductors because of additional difficulties of carrier injection from electrodes as a result of very low highest occupied molecular orbital (HOMO) and/or very high lowest unoccupied molecular orbital (LUMO) levels.9

To address this problem, most recent molecular designs focus on bipolar wide bandgap materials by the incorporation of electron-donating and electron-accepting moieties.¹⁰ Although the HOMO and/or LUMO are raised and/or lowered by this strategy, respectively, it also unavoidably lowers the bandgap of the material due to decrease of the HOMO–LUMO bandgap or intramolecular charge-transfer between the electrondonating and electron-accepting moieties.¹¹ Thus, there remains a need to develop a novel molecular design strategy to optimize the optical bandgap and carrier injection simultaneously. In this communication, we describe here a strategy to achieve this goal through a substituted silane with electron-donating (carbazole)

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and electron-accepting (pyridine) moieties on the basis of photophysical, electrochemical measurements and density functional calculations. The visual illumination as shown in Fig. 1 expresses our basic strategy of independently adjusting electrical and optical bandgaps. The HOMO and LUMO levels of the unsubstituted silane are around 6.2 eV and 2.0 eV, respectively, resulting in a very difficult injection of carriers.¹² While for the substituted silane, the HOMO and LUMO are mainly located on corresponding electron-donating and electronaccepting moieties, respectively. This results in a lower electrical bandgap compared with unsubstituted silane. Meanwhile, the larger and "insulating" spacer, the tetraphenylsilane moiety, leads to forbidden electronic transitions between a donor and an acceptor (from HOMO to LUMO). The allowed electronic transitions are excited from HOMO to higher energy levels of LUMO + n. Therefore, the whole molecule would maintain a wide optical bandgap. This strategy suggests that we could use different energy levels to control the electrical bandgap and optical bandgap in one molecule.



Fig. 1 A schematic representation of the design principle for bipolar wide bandgap materials and molecular structures of the wide bandgap materials.

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Fig. 2 Cyclic voltammogram (a) and the HOMO–LUMO levels (b) of the wide bandgap materials. The oxidation and reduction processes were performed in CH_2Cl_2 and DMF solution, respectively.

The chemical structures of these wide bandgap materials are also shown in Fig. 1. Detailed synthesis procedures of these compounds are presented in ESI.† The final molecular structures were characterized by ¹H NMR, ¹³C NMR, mass spectrometry, elemental analysis, and corresponded well with their expected structures.

Cyclic voltammetry (CV) was used to determine the relative energy levels of these newly synthesized compounds. Because of the strong electron-donating and electron-accepting abilities of carbazole and pyridine, the redox properties of the substituted silanes were obviously changed. This can be seen from Fig. 2a, in which the reductive onset potential positively shifts from -2.64 V for silane to -2.23 V for pyridine substituted SiPy, and oxidative onset potential negatively shifts from 1.71 V for silane to 1.11 V for carbazole substituted CzSi. While the D-A compound CzSiPy, exhibiting a combination of the reduction behavior of SiPy and the oxidation behavior of CzSi, shows the bidirectional shifts of onset potentials caused by carbazole and pyridine substituents. On the basis of the onset potentials for reduction and oxidation, we estimated the LUMO and HOMO energy levels of these compounds with regard to ferrocene (-4.80 eV below vacuum). The HOMO/LUMO levels diagram of these compounds is demonstrated in Fig. 2b. It is evident that all the D-A silanes have lower LUMO levels and higher HOMO levels compared with unsubstituted silane, suggesting smaller carrier-injection barriers from neighboring layers or electrodes to these materials.

If such D-A substitution induces a great red-shift in spectra (lowering bandgap), the design strategy may be useless for wide bandgap materials. Surprisingly, we found from spectral measurements that unlike a great change in redox properties, the D-A silanes showed almost the same absorption and PL spectra as their corresponding carbazolsilanes. As shown in Fig. 3a, they all exhibit major absorption around 293 nm and 342 nm. And the molar absorption coefficients of the D-A silanes are close to that of their corresponding carbazole substituted silanes, showing increase as a function of the number of carbazole groups (Table S1, ESI[†]). Longer wavelength absorptions in the low energy region are not observed for CzSiPy, DCzSiPy and TCzSiPy, which means that additional transitions, such as the intramolecular charge-transfer (ICT) from carbazole to pyridine, do not exist in CzSiPy, DCzSiPy and TCzSiPy. With the carbazole substituents changing from a carbazole monomer to a carbazole dimer, and further to a trimer, the PL spectra of these compounds red-shift (Fig. 3b), which is attributed to the extension of delocalization arising from the partial electronic coupling of oligocarbazoles. However, the main emission peaks of TCzSi



Fig. 3 UV spectra (a) and PL spectra (b) of the wide bandgap materials in dichloromethane solution (10^{-5} M) .

and TCzSiPy are still shorter than 400 nm (3.22 eV). From the analysis above, we can unhesitatingly consider that the optical transitions and radiations of CzSiPy, DCzSiPy and TCzSiPy are dominated by their carbazole chromophore, while the pyridine unit does not have effects on the absorption and emission spectra. Thus the bandgap of all the materials, calculated from the lowest absorption peak of the film (Fig. S2 in the ESI†), maintains high values ranging from 3.58 to 3.62 eV.

Density functional theory (DFT) calculations at the B3LYP/6-31G* level are performed to characterize the threedimensional geometries, the frontier molecular orbital energy levels and transitions in order to reveal the origin of special spectral behaviors. Taking CzSiPy as an example, Fig. 4 shows the relevant molecular orbitals (MOs) of CzSiPy involved in the ground-state. The HOMO of CzSiPy is mainly located on the electron donating carbazole moiety, while the LUMO is mainly distributed on the electron-accepting pyridine moiety as anticipated, which are consistent with the CV measurement results. The geometrical characteristics of CzSiPy depict obviously that the HOMO and LUMO orbitals are significantly separated from each other because of the tetrahedral environment of the central tetraphenylsilane, which plays a role of "insulating" bridge. Thus this full spatial separation for HOMO and LUMO configurations leads to no overlap of the MOs involved with an oscillator strength of zero, demonstrating the forbidden character of the transitions between the donor and acceptor (from HOMO to LUMO). While the allowed singlet transition is found to be from HOMO to higher energy levels LUMO + 2 in the ground state.



Fig. 4 The relevant molecular orbitals density map and the transition sketch map of CzSiPy calculated at the B3LYP/6-31G* level.

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This local transition makes CzSiPy to maintain a high level of optical bandgap. Similar to CzSiPy, the DCzSiPy and TCzSiPy showed the same excited state properties investigated *via* DFT analysis. This special optical phenomenon provides these materials with sufficient bandgap.

One of the important applications of organic wide bandgap materials is their use as host materials for phosphorescent dyes in POLEDs. Because efficient exothermic energy transfer from the host materials to the dopant phosphorescent dye depends on whether the triplet-state energy of the host is greater than that of the dopant, a higher level of triplet energy $(E_{\rm T})$ for the host material is required to allow the effective confinement of triplet excitons on the guest.¹³ CzSi and CzSiPy show phosphorescence peaks at 415 and 402 nm, which correspond to the vibronic 0-0 transition between these two electronic states by taking the highest-energy peak of phosphorescence as the transition energy of T1 \rightarrow S0.¹⁴ Thus, the triplet energies of CzSi and CzSiPy are estimated to be as high as 2.99 and 3.08 eV, respectively. With the same method, the triplet energies of other compounds are estimated to be all above 2.86 eV, which are higher than the commonly used blue dye FIrpic (2.65 eV).¹⁵ The results show that the effect of the pyridine unit on the $E_{\rm T}$ is negligible, which is consistent with the singlet spectral investigation. In this case, the $E_{\rm T}$ is high enough for these compounds to serve as a decent host.

We primarily investigated the potential of these compounds as hosts for POLEDs. For a blue emitter, FIrpic, doped devices with a configuration of ITO/PEDOT/NPB (80 nm)/ mCP (30 nm)/host:FIrpic (100:16, 30 nm)/TPBI (50 nm)/ LiF/Al are fabricated. The device using DCzSiPy as the host demonstrates the best performance, showing a turn-on voltage (at 1 cd m⁻²) of 3.4 V and a maximum brightness of 33 000 cd m⁻² at 17 V. The little high turn-on voltage of the devices may be attributed to the much thicker device film. Its maximum luminous efficiency is 18.1 cd A^{-1} , which is 23% greater than that of a DCzSi-based device. Normalized electroluminescence (EL) spectra at a brightness of 100 cd m⁻² show the emission exclusively from FIrpic, no emission from the host was observed, indicating that the triplet energy levels of these compounds are high enough to prevent the backward energy transfer from FIrpic. More efficient devices are expected by further optimization of the device structure.

In summary, we have developed a new molecular design strategy for organic wide bandgap materials with a special molecular structure, using silane to couple electron-donor and electron-acceptor units. Following this idea, a series of tetraarylsilane-centered compounds CzSiPy, DCzSiPy and TCzSiPy are synthesized. A thorough experimental and theoretical study of these materials leads to the following conclusions for this molecular design strategy: (i) the HOMO/LUMO levels of the compounds mainly depend on the electron-donating and electron-accepting moieties, respectively, thus we could freely tune the HOMO/LUMO levels of the materials by incorporating different substituent groups. (ii) The tetraphenylsilane core not only interrupts the conjugation of the compounds but also avoids the intramolecular chargetransfer (ICT) from a donor to an acceptor. Consequently, the optical bandgaps of the compounds are determined by local excitations of substituents. Therefore, the whole molecule could maintain a wide optical bandgap. This novel strategy gives us a hopeful prospect for organic wide bandgap materials design to achieve optimization of not only wide bandgap (both high singlet and triplet energies) but also favorable energy levels for charge injection from neighboring layers or electrodes.

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