Organic Electronics

Oligosiloxane Functionalized with Pendant (1,3-Bis(9carbazolyl)benzene) (mCP) for Solution-Processed Organic Electronics

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Abstract: A new oligosiloxane derivative (ODCzMSi) functionalized with the well-known 1,3-bis(9-carbazolyl)benzene (mCP) pendant moiety, directly linked to the silicon atom of the oligosiloxane backbone, has been synthesized and characterized. Compared to mCP, the attachment of the oligosiloxane chain significantly improves the thermal and morphological stabilities with a high decomposition temperature (T_{g} = 540 °C) and glass transition temperature (T_{g} = 142 °C). The silicon–oxygen linkage of ODCzMSi disrupts the backbone conjugation and maintains a high triplet energy level (E_{T} = 3.0 eV). A phosphorescent organic light-emitting diode (PhOLED) using iridium bis(4,6-difluorophenyl)pyridinato-N,C² picolinate (FIrpic) as the emitter and ODCzMSi as the host shows a relatively low turn-on voltage of 5.0 V for solution-processed PhOLEDs, maximum external quantum effi

Introduction

Carbazole-based optoelectronic materials continue to attract widespread attention for their hole-transporting properties, good thermal stability and versatile chemical modification.^[1-7] Typically, the semiconductor poly(*N*-vinylcarbazole) (PVK) the good hole-transporting properties of which are attributed to the intra-chain π - π stacking alignment, has been widely used in organic photoconductive materials,^[8] as the host material for green OLEDs and blue phosphorescent OLEDs,^[9–14] and conductance switching materials.^[15–18] However, PVK forms exciplexes and triplet trap states which can quench blue emission

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ciency of 9.2%, and maximum current efficiency of 17.7 cd A⁻¹. The overall performance of this device is competitive with the best reported solution-processed blue PhO-LEDs. Memory devices using ODCzMSi as an active layer exhibit non-volatile write-once read-many-times (WORM) characteristics with high stability in retention time up to 10^4 s and a low switch on voltage. This switching behaviour is explained by different stable conformations of ODCzMSi with high or low conductivity states which are obtained under the action of electric field through a π - π stacking alignment of the pendant aromatic groups. These results with both PhOLEDs and memory devices demonstrate that this oligosiloxane–mCP hybrid structure is promising and versatile for high performance solution-processed optoelectronic applications.

of PhOLEDs and the precise triplet level of PVK is ambiguous;^[19] moreover, its low-lying HOMO energy level (-5.9 eV) and high resistivity lead to a high operating voltage, so it is far from an ideal host material.^[20] As a conductance switching material, PVK has an aliphatic hydrocarbon backbone that exhibits low dimensional stability. For another example, 1,3-bis(9-carbazolyl)benzene (mCP) is one of the major milestones as a smallmolecule host of choice for vacuum deposited blue PhO-LEDs.^[21,22] mCP has the benefits of a simple molecular structure and a triplet energy of 3.0 eV. However, mCP has the drawbacks of low thermal and morphological stability (with a glass transition temperature T_{α} of only 60 °C) which limit its use in high-performance blue PhOLEDs for real applications and commercialization. Thus, it remains a great challenge to develop new materials with high thermal, electrochemical, and morphological stability, and good film-forming ability as hosts for PhOLEDs and as active layers in non-volatile memory devices.

From this viewpoint, functionalized PVK derivatives show improved electron-transporting ability, thermal and morphological stabilities as compared to PVK, such as poly(*N*-vinyl-3-(9-phenylfluoren-9-yl)carbazole (PVPFK).^[17,23,24] Efforts have also been made to improve the thermal stability of mCP while still maintaining the molecules' desirable optoelectronic properties.^[21,25-27] Organic–inorganic hybrid materials are one of the best solutions for ideal host materials because the functionality

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and structural strength are easily achieved by design of the organic and the inorganic parts, respectively.^[28–33] For instance, 3,5-di(*N*-carbazolyl)tetraphenylsilane (SimCP) is a good host for blue PhOLEDs: by linking the bulky triphenylsilyl group to the carbazole moiety in a non-conjugated way, the thermal stability is improved and steric hindrance favourably affects the molecular packing in the condensed phase.^[35,36]

Polysiloxanes are a fascinating class of organosilicon polymers with good solubility in common organic solvents, good film-forming ability, fair adhesion to various substrates and excellent resistance to thermal, chemical and irradiation degradation. To improve thermal, electrochemical, and morphological stability and film-forming ability of organic semiconductors, incorporation of siloxanes into organic molecular structures has been successful.^[30] This strategy does not significantly affect the electronic properties of the organic semiconductor units. Strohriegl synthesized a side-chain carbazole polymer with a siloxane main chain (PSX), which displays better performance than PVK, including greater conformational freedom, good solution processability and minimized excimer formation upon photoexcitation.^[36] However, this method adopted a common synthetic pathway to post-polymerization functionalization which gave a low content of carbazole groups in the polymer chains, which would not be applicable in high performance conductance switching materials.

Herein, we successfully incorporate 1,3-bis(9-carbazolyl)benzene (mCP) moieties into oligosiloxane chains as pendant groups to obtain the new mCP modified oligosiloxane (ODCzMSi). ODCzMSi possesses a sufficiently high E_{T} of 3.0 eV because the silicon-oxygen bond interrupts π -conjugation in the polymer main chain.^[37-39] This material discourages selfquenching of triplet excitons by preventing phosphorescent dyes from aggregating. In addition, ODCzMSi possesses a high degradation temperature, excellent film-forming ability and good compatibility with the standard blue phosphorescent emitter FIrpic. An efficient blue PhOLED with a solution-processed emitting layer of ODCzMSi host and Flrpic (10% by weight) displayed a maximum current efficiency of 17.7 cd A⁻¹ (7.7 Im W^{-1} , external quantum efficiency 9.2%) at 1306 cd m⁻². Additionally, memory devices using ODCzMSi as the active layer exhibit non-volatile write-once read-many-times (WORM) characteristics with low turn-on threshold voltages. ODCzMSi has, therefore, the very attractive properties of both a solutionprocessable host for blue PhOLEDs and an active material for memory devices, indicating its considerable versatility in organic electronics.

Results and Discussion

Synthesis and characterization

The synthetic route of ODCzMSi (4) is depicted in Scheme 1. The starting material 9,9'-(5-bromo-1,3-phenylene)bis(9H-carbazole) (1) was synthesized by a modified Ullmann condensation of carbazole with 1,3,5-tribromobenzene in the presence of copper(I) iodide as a catalyst and 18-crown-6 as a ligand in *o*dichlorobenzene. Transformation of 1 into the diethoxy(methyl)silyl-derivative 2 was achieved by a Barbier-Grignard reaction with methyldiethyoxylchlorosilane. (3,5-Di(9H-carbazol-9-yl)phenyl)(methyl)silanediol (3) was obtained by subsequent acid hydrolysis in dilute THF/HCl solution at 0°C. The desired oligomer 4 was easily synthesized from the corresponding diethoxy monomer (OEt-Si) and dihydroxy monomer (OH-Si) under tetrabutyl titanate (TBOT) catalysed polycondensation as described in the Experimental Section. The end groups were blocked with trimethylchlorosilane to stabilize the resultant oligosiloxane. After completion of the reaction, the solution was simply concentrated and the product 4 precipitated in methanol as a white powder, which was characterized by ¹H, ²⁹Si NMR spectroscopies and gel permeation chromatography (GPC). The weight average molecular weight was determined to be 2.13 kDa with a narrow polydispersity index of 1.13 by GPC in THF using polystyrene as a standard. Product 4 is highly soluble in common organic solvents such as chloroform, tetrahydrofuran, toluene and chlorobenzene. Therefore, it can be easily fabricated into films by solution casting, spincoating and dipping techniques which are advantageous for organic electronics applications.^[40]

Thermal analysis

The thermal properties of OCzMSi were characterized by thermal gravimetric analysis (TGA) and differential scanning calo-



Scheme 1. Synthetic route for ODCzMSi (4).

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Table 1. Physical properties of ODCzMSi.									
E _T [eV] ^[a]	HOMO [eV] ^[b]	LUMO [eV] ^[c]	<i>T</i> _g [°C] ^[d]	τ _d [°C] ^[e]					
3.0	-5.65	-2.09	142	540					
[a] Triplet energy level. [b] Highest occupied molecular orbital. [c] Lowest unoccupied molecular orbital. [d] Glass-transition temperature determined by DSC. [e] Decomposition temperature determined by TGA at 5% weight loss.									

rimetry (DSC) under a nitrogen atmosphere and are summarized in Table 1.

As shown in Figure 1, the decomposition temperature (T_d) , which corresponds to a weight loss of 5% at a heating rate of $10 \,^{\circ}\text{C}\,\text{min}^{-1}$ during TGA, was measured as 540 °C for ODCzMSi, which implies that the material has very good thermal stability. Meanwhile, a higher glass transition temperature (T_g) of $142 \,^{\circ}\text{C}$ (compared to $60 \,^{\circ}\text{C}$ for mCP) was determined by DSC during the second heating cycle. In addition, no exothermic crystallization or endothermic melting peaks were observed from 40 to 200 °C, suggesting that amorphous ODCzMSi should exhibit high morphological stability in a device. The excellent thermal stability of ODCzMSi is ascribed to the oligosiloxane backbone, which should be capable of enduring the inevitable Joule heating that occurs during device operation.



Figure 1. a) TGA trace of ODCzMSi recorded at a heating rate of 10° Cmin⁻¹. b) DSC measurement recorded at a heating rate of 10° Cmin⁻¹.

Morphology properties

The film-forming ability, morphological stability of ODCzMSi and its compatibility with the dopant FIrpic were investigated by atomic force microscopy (AFM). As shown in Figure 2a, the AFM image of 10 wt% FIrpic doped into ODCzMSi film displays

smooth and homogeneous morphology with a small value of root-mean-square (RMS) roughness of 0.33 nm. It is free of particle aggregation or phase separation, suggesting both good film-forming ability and good miscibility with the Flrpic. To further investigate the thermal stability, the film was then annealed at 140 °C, which is almost the same temperature as with the corresponding T_g of ODCzMSi, for 12 h. As shown in Figure 2b, the surface roughness changed a little from 0.33 to 0.48 nm, however, with increasing time (up to 48 h) at the same temperature, no further change can be observed (Figure 2c and d). The excellent stability of the film morphology, which is due to the siloxane backbone, means that films should retain their integrity throughout the fabrication and device-operation processes.



Figure 2. AFM topographical images of the solution-processed films of ODCzMSi doped with 10% FIrpic: a) unannealed, b) annealed at 140 °C for 12 h, c) annealed at 140 °C for 24 h, and d) annealed at 140 °C for 48 h.

Photophysical properties

UV/Vis absorption, photoluminescence (PL; recorded at room temperature) and phosphorescence spectra (recorded at 77 K) of ODCzMSi in dilute dichloromethane solution are presented in Figure 3 a. The absorption peaks in the UV/Vis spectrum at around 293 nm can be assigned to $\pi \rightarrow \pi^*$ transitions of the carbazole moiety and weaker absorption peaks at longer wavelengths of 326 and 339 nm are attributed to the $n \rightarrow \pi^*$ transitions of extended conjugation of the carbazole moiety.^[25] In addition, a relatively wide energy gap (E_{o}) of 3.56 eV is obtained from the onset of absorption. The photoluminescence (PL) spectrum of displays intense UV emission peaks at 346 and 363 nm. The absorption and emission spectra of ODCzMSi are nearly identical to those previously reported for phenylcarbazole structure and mCP^[38, 39, 41-43] suggesting that the oligosiloxane backbone does not significantly influence the photophysical properties of the organic chromophore. The phosphorescence spectrum in a frozen dichloromethane solution at 77 K revealed a well-structured band in the region of 400-500 nm. An E_{T} of 3.0 eV was calculated from the highest energy vibronic sub-band of the phosphorescence spectrum;

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Figure 3. a) Absorption, photoluminescence (at room temperature) and phosphorescence spectra (at 77 K) of ODCzMSi in dichloromethane. b) Cyclic voltammogram of ODCzMSi in CH_2CI_2 for oxidation scan.

this is the same value as mCP and is consistent with the disruption of π conjugation caused by the silicon–oxygen bond between the mCP groups.

Electrochemical analysis

The electrochemical behaviour of ODCzMSi was investigated by cyclic voltammetry (CV) using tetra(n-butyl)ammonium hexafluorophosphate (0.1 M) as a supporting electrolyte in anhydrous acetonitrile under a nitrogen atmosphere. In Figure 3b, the CV shows an irreversible oxidation feature similar to those of other carbazole derivatives with unprotected 3,6-positions.^[16,28] The highest occupied molecular orbital (HOMO) energy level of ODCzMSi was calculated according to the formula $E_{HOMO} = -(4.8 + E_{ox}^{on} - E_{Fc}) \text{ eV.}^{[29]}$ The lowest unoccupied molecular orbital (LUMO) energy level was obtained by adding the optical E_{a} to the HOMO level (as shown in Table 1). The HOMO level of ODCzMSi is -5.65 eV, which is very similar to that of mCP and 4,4'-N,N'-dicarbazolylbiphenyl (CBP).^[44] This indicates that the HOMO of ODCzMSi is mainly located at the electron-rich carbazole units. Quantum chemical calculations on a dimer model of ODCzMSi at the B3LYP/6-31G* level gave the contour plots depicted in Figure 4. The HOMO is localized on the carbazole group, while the LUMO is mainly localized on the phenyl group attached to the carbazole. There is no frontier molecular orbital distribution on the silicon-oxygen bond. All the above data establish that the presence of the siloxane chain has a negligible effect on the electronic transition energies and energy levels of the mCP units, thus maintaining the





Figure 4. Calculated spatial distributions of the HOMO and LUMO energy densities of ODCzMSi.

desirable properties of mCP while significantly enhancing the thermal and morphological stability of the material.

Blue phosphorescent organic light emitting diode

To evaluate the ability of ODCzMSi to act as a host material for solution-processed blue PhOLEDs, we chose FIrpic $(E_T 2.6 \text{ eV})^{[45]}$ as the standard blue phosphor. Devices were fabricated with the following configuration: indium tin oxide (ITO)/PEDOT:PSS (40 nm)/host/10 wt% FIrpic (40 nm)/1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene (Tm3PyPB, 5 nm)/1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi, 30 nm)/LiF (1 nm)/Al (100 nm). In this architecture, PEDOT:PSS acts as a hole-injection layer, the host doped with 10 wt % FIrpic is spin-coated to form an emitting layer, and Tm3PyPB^[46] and TPBi function as the hole/excitonblocking and electron transporting layers, respectively. The relative energy levels of each layer are presented in Figure 5a. The E_{T} values of ODCzMSi and Tm3PyPB are sufficiently high to prevent luminescence quenching by the carrier transport layer and to confine triplet excitons in the emitting layer. As shown in Figure S1 in the Supporting Information, the electroluminescent (EL) spectra of the blue PhOLED shows emission exclusively from FIrpic ($\lambda_{max} = 472 \text{ nm}$), without any contribution from ODCzMSi. This indicates that reverse transfer of triplet excitons from phosphor to host is prevented in this device. Importantly, a stable emission spectrum is observed throughout the operating voltage (6-10 V). The intensity of the emission shoulder around 500 nm increases when the charge recombination zone shifts to the side of the hole-transporting layer. As the operating voltage increased, the intensity of this shoulder is enhanced, which indicates that the emission zone is shifted away from the electron-transporting layer because of the improved electron flow.

It is notable that the highest external quantum efficiency for the device is 9.2% as shown in Figure 5 c. Power and current efficiencies plotted with respect to current density are depicted in Figure 5 d, and all the device data are summarized in Table 2. The device shows a current efficiency of 17.7 cd A⁻¹ and maximum power efficiency of 7.7 lm W⁻¹, which are observed over a wide range of high luminance. The overall performance of this device is excellent and is competitive with the best blue PhOLEDs using solution processed host materials.^[47,48] The efficiency is considerably enhanced compared to analogous optimized Flrpic devices with PVK as the host, which gave maximum values of 1640 cd m⁻²; 6.3 cd A⁻¹; 3.3 lm W⁻¹; η_{ext} 3.3%.^[14]

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Figure 5. a) Relative energy levels of the materials used in the 10 wt % FIrpic-doped PhOLED; b) *J–V–L* characteristics; c) external quantum efficiency versus current density; d) power efficiency and current efficiency versus current density.

Table 2. Performance of the FIrpic-ODCzMSi-based PhOLED device.									
V_{on} $[V]^{[a]}$	L_{max} $[cd m^{-2}]^{[b]}$	$\eta_{c,max}$ [cd A ⁻¹] ^[c]	$\eta_{ m p,max}$ $[{ m Im}{ m W}^{-1}]^{[{ m d}]}$	$\eta_{ m ext,max}$ $[\%]^{[e]}$	$CIE(x,y)^{[f]}$				
5.0	4730	17.7	7.7	9.2	0.15,0.33				
[a] Turn-on voltage, measured at a brightness of 1 cd m ⁻² . [b] Maximum luminance. [c] Maximum luminous efficiency. [d] Maximum power efficiency. [e] External quantum efficiency. [f] Commission Internationale de l'Éclairage coordinates measured at 8 V.									

To further verify the exciton confinement property of the host, transient photoluminescence decays were measured at a wavelength of 475 nm for a thin film (formed on quartz substrates) with 10 wt% Flrpic dispersed in ODCzMSi. As shown in Figure 6, the emission displays nearly mono-exponential decay curves, indicating that the triplet energy transfer from Flrpic to ODCzMSi is completely suppressed and the energy is well confined in the emission layer. Meanwhile, the decay curve of the corresponding film annealed at 140 °C for 24 h was essentially unchanged which is consistent with high thermal stability of the Flrpic-ODCzMSi film.

Memory device characteristics

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To investigate the applicability of ODCzMSi in non-volatile memory devices, we fabricated a sandwich device with a configuration of ITO/ODCzMSi/Au. Figure 7 shows the typical current density-voltage (J-V) characteristics and stability tests of this device. As depicted in Figure 7a, the device could be switched on when a negative voltage sweep (with ITO as cath-



Figure 6. Transient photoluminescence decay (excited at 343 nm) curves at room temperature monitored at 475 nm for the unannealed 10 wt % Flrpic co-deposited with ODCzMSi, and the corresponding film annealed at 140 °C for 24 h.

5), meeting the features of a WORM (write-once-read-manytimes) device. Further experiments on duplicated devices revealed that the J-V characteristics were repeatable with good accuracy, and device degradation was not observed. Furthermore, the almost linear current-area dependence of both the OFF- and ON-states when the active device area was reduced (Au electrode)—giving almost constant current densities—indicates the absence of sample degradation and dielectric breakdown. The observed conductance switching can thus be fully attributed to the change in the material properties of the ODCzMSi layer upon applying an external bias. It is noteworthy that the on-switching voltage was only -0.91 V which facilities

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ode and Au as anode) was applied. Initially a low-conductivity (OFF) state (current density level $\sim 10^{-6} \text{ mA cm}^{-2}$) was observed. As the negative bias increased, a sharp transition from the lowconductivity (OFF) state to a high-conductivity (ON) state was observed at -0.91 V (the switch-ON voltage), as indicated by the abrupt increase in the current density (sweep 1). For a memory device, this transition from the OFF- to the ON-state could serve as the "writing" process for practical data storage applications. Once the device has reached its ON-state, it could retain its ON-state when the voltage sweep was repeated from 0 to -3 V (sweep 2). Even when the power was shut off or the reverse durina voltage sweep (sweep 3), the ON-state was still retained (sweeps 4 and

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sibility of the process confirms

change mechanism. In addition,

comparing this non-volatile elec-

trical switching behaviour of the

annealed device with that of the

non-written device, some differ-

ence was observed. With a nega-

tive bias sweep, the switching

voltage is slightly increased to

around -1.01 V and the ON/OFF

current density ratio is increased

to about 7×10^3 as shown in Fig-

ure 8 a and b. With a positive

bias sweep, the switching volt-

age is slightly increased to

around 1.59 V and the ON/OFF

current density ratio is almost

the same as shown in Figure 8c

and d. The different switching

voltages and ON/OFF current density ratios may be attributed

to the different initial states of

the annealed device and the

non-written device, which have

different regio-regularity of the

PDCzMSi chains.

conformation

proposed

low-power consumption. The electrical stability performance was also carried out for the memory device under ambient air conditions. Figure 7b shows the retention time test under a constant voltage for the OFF- and ON-states. Under a constant bias of -0.5 V, no significant degradation in current is observed for both the ON- and OFF-states with longer operating time (8000 s); the device maintained an ON/OFF current ratio of about 2.5×10^3 . Moreover, this non-volatile irreversible electrical switching behaviour was also observed when scanning the device first with positive bias (with ITO as anode and Au as cathode), indicating its independence on the voltage polarity. However, the switching voltage is slightly increased to around 1.26 V and the ON/OFF current density ratio is reduced to about 300, as shown in Figure 7 c and d.

conductivity states. The regular π - π stacking conformation of the high-conductivity states should be converted into a disordered state by thermal annealing. Thus, we chose 140 °C, which is close to the T_g of ODCzMSi where its chain segments should have higher flexibility. When the device with high-conductivity states was annealed at 140 °C for 12 h, the previous sustained high-conductivity (ON) state disappeared as shown in Figure 8. Instead its initial low-conductivity (OFF) state from 0 V to -1.01/1.59 V is observed, and then there is a sharp increase, indicating another transition of the device from the low-conductivity to a high-conductivity state. Once the annealed device is switched on, it remains there and cannot be returned to its initial low conductivity state. This suggests that the stored data can be erased by thermal treatment. The rever-

the



Figure 7. Typical *J*–*V* curves of the ITO/ODCzMSi/Au memory device. The sweep sequence and direction are indicated by the number and arrow, respectively. a) Sweep numbers 1, 2, 4: 0 to -3 V; sweep numbers 3, 5: 0 to +3 V; c) sweep numbers 1, 2, 4: 0 to +3 V; sweep numbers 3, 5: 0 to -3 V. The effect of operation time on the current density of the device at the ON- and OFF-states tested at different biases under ambient conditions: b) -0.5 V; d) 0.5 V.

Conformation induced electrical switching mechanism can satisfactorily explain the electrical switching behaviour of ODCzMSi. There are literature precedents for the electrical bistability of some non-conjugated polymers with pendant active groups.^[49–51] For example, memory effects of PVK derivatives with flexible spacers between the carbazole pendant group and the polymer backbone,^[16,17] in which regio-random and regio-regular alignments correspond to the low- and high-conductivity states, showed only WORM or volatile features. Similarly, different stable conformations of ODCzMSi with high or low conductivity states could be obtained under the action of electric field through the π - π stacking alignment of its pendent aromatic groups inducing the electrical switching performance.

The proposed mechanism of conformation change is supported by annealing the ITO/ODCzMSi/Au device with high-

Conclusion

In summary, a solution-processable oligosiloxane derivative has been designed and synthesized by attaching the mCP moiety to the oligosiloxane backbone. Compared to mCP, ODCzMSi exhibits excellent thermal and morphological stability. Because the mCP segments are connected through silicon–oxygen bonds that disrupt the π conjugation, ODCzMSi maintains a high $E_{\rm T}$ of 3.0 eV. A highly efficient blue PhOLED with maximum external quantum, current and power efficiencies of 9.2%, 17.7 cd A⁻¹, and 7.7 lm W⁻¹, respectively, was fabricated using ODCzMSi as the host material and FIrpic as the triplet emitter. Moreover, memory devices using PDCzMSi as an active layer exhibited non-volatile memory performance with high stability in retention time up to 8000 s and low switch on volt-

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Figure 8. The ITO/ODCzMSi/Au memory device in its high-conductivity states is annealed at 140 °C for 12 h and then the device properties are determined again. Typical *J*–*V* curves of the annealed memory device, the sweep sequence and direction are indicated by the number and arrow, respectively. a) Sweep numbers 1, 2, 4 :0 to -3 V; sweep numbers 3, 5: 0 to +3 V; c) sweep numbers 1, 2, 4: 0 to +3 V; sweep numbers 3, 5: 0 to -3 V. The effect of operation time on the current density of the device at the ON- and OFF-states tested at different biases under ambient conditions: b) -0.5 V; d) 0.5 V.

age. These results demonstrate the great promise and versatility of organic–inorganic hybrid materials for organic electronics applications.

Experimental Section

Materials

The intermediate methyldiethyoxylchlorosilane was prepared according to our previous report.^[52] All reactants (Adamas-beta) were purchased from Adamas Reagent, Ltd. without further purification, and all solvents were supplied by Beijing Chemical Reagent Co., Ltd. Anhydrous and deoxygenated solvents were obtained by distillation over sodium benzophenone complex.

Molecular simulation

The geometrical and electronic calculations were carried out on the dimer of PDCzMSi with the Gaussian 09 program package.^[53] The molecular orbitals were calculated by the density functional theory (DFT) method at the B3LYP level with the 6–31G(d) atomic basis set.

Device fabrication

PhOLEDs

The configuration used is: indium tin oxide (ITO)/PEDOT/PSS (40 nm)/ODCzMSi/10 wt% FIrpic (40 nm)/1,3,5-tri(*m*-pyrid-3-yl-phe-nyl)benzene (Tm3PyPB, 5 nm)/1,3,5-tris(1-phenyl-1*H*-benzimidazol-2-yl)benzene (TPBi, 30 nm)/LiF (1 nm)/Al (100 nm). The hole-injec-

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tion material PEDOT/PSS, and electron-transporting and hole-blocking material TPBi, were used from commercial sources. ITO-coated glass with a sheet resistance of 10 Ω square⁻¹ was used as the substrate. Before device fabrication, the ITO-coated glass substrate was pre-cleaned carefully and exposed to UV-ozone for 2 min. After that, PEDOT/PSS was spin-coated onto the clean ITO substrate as a hole-injection layer. Then, the host ODCzMSi doped with 10% (by weight) FIrpic was spin-coated to form a 40 nm thick emissive layer (EML) and annealed at 100 °C for 30 min to remove residual solvent. Finally a 5 nm thick holeblocking layer (HBL) of Tm3PyPB and a 30 nm-thick electron-transporting layer (ETL) of TPBi were vacuum deposited, and for the cathode of a 1 nm thick layer of lithium fluoride (LiF) and aluminum (100 nm) were sequentially deposited onto the substrate through shadow masking with a pressure of 10⁻⁶ Torr. The current densityvoltage-luminance (J-V-L) characteristics of the device was measured using a Keithley 2400 Source meter and a Keithley 2000 Source

multimeter equipped with a calibrated Si-photodiode in a glove box. The EL spectra were measured using a JY SPEX CCD 3000 spectrometer. The EQE values were calculated from the luminance, current density, and electroluminescence spectrum according to previously reported methods.^[54] All measurements were performed at room temperature under ambient conditions.

Memory device

The memory devices with the configuration of ITO/ODCzMSi/Au were fabricated as follows. ITO-coated glass with a sheet resistance of 10 Ω square⁻¹ was used as the substrate. Before device fabrication, the ITO-coated glass substrate was pre-cleaned carefully. After that ODCzMSi was spin-coated onto the ITO glass substrate. Finally, an Au top electrode was sputter coated onto the active layers through a shadow mask at a system pressure of 10⁻³ bar. The current density–voltage (*J–V*) characteristics of the sandwich devices were recorded with a Keithley 4200 SCS semiconductor parameter analyser (Keithley, Cleveland, OH) equipped with a Micromanipulator 6150 probe station in a clean and metallically shielded box in an ambient environment.

Characterization

¹H and ¹³C NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer. Chemical shifts (δ) are given in parts per million (ppm) relative to tetramethylsilane (TMS; δ = 0) as the internal reference. ¹H NMR spectral data are reported as chemical shift, relative integral, multiplicity (s=singlet, d=doublet, m=multiplet), coupling constant (*J* in Hz) and assignment. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario EL

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cube. UV/Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. PL spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was performed on a TA Q2000 Differential Scanning Calorimeter at a heating rate of 10°Cmin⁻¹ from 25 to 200°C under nitrogen atmosphere. The glass transition temperature (T_q) was determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken with a METTLER TOLEDO TGA/DSC 1/1100SF instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 10°C min⁻¹ from 25 to 800°C. Cyclic voltammetry (CV) was carried out in nitrogen-purged dichloromethane (oxidation scan) at room temperature with a CHI voltammetric analyser. Tetrabutylammonium hexafluorophosphate (TBAPF₆; 0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/AgNO₃ pseudo-reference electrode with ferrocenium-ferrocene (Fc⁺/Fc) as the internal standard. Cyclic voltammograms were obtained at scan rate of 100 mV s⁻¹. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram. Gel permeation chromatography (GPC) analysis was carried out on a Waters 515-2410 system using polystyrene standards as molecular weight references and tetrahydrofuran (THF) as the eluent. The morphologies and thickness of the oligomer films coated on the ITO substrate were measured using atomic force microscopy (Agilent-5500 AFM) under tapping mode.

Synthetic procedures

9,9'-(5-Bromo-1,3-phenylene)bis(9H-carbazole)

A mixture of carbazole (16.7 g, 100 mmol), 1,3,5-tribromobenzene (15.7 g, 50 mmol), Cul (0.95 g, 5 mmol), 18-crown-6 (2.0 g, 7.5 mmol), potassium carbonate (36.6 g, 150 mmol), and o-dichlorobenzene (200 mL) was de-gassed and stirred at 180°C for 24 h under argon. After cooling to room temperature, the mixture was quenched with saturated (NH₄)₂CO₃ solution and extracted with chloroform; the combined organic layer was washed with distilled water three times and dried over anhydrous magnesium sulfate. Then the solvent was evaporated in vacuum to give the crude product, which was purified by column chromatography on silica gel using (petroleum ether/dichloromethane=60:1 v/v) as the eluent to obtain the product as a white solid (11.9 g, 49%). ¹H NMR (400 MHz, $[D_8]$ THF): $\delta = 7.36$ (t, J = 7 Hz, 4H; Ar H), 7.49 (t, J = 7 Hz, 4H; Ar H), 7.57 (d, J=8 Hz, 4H; Ar H), 7.82 (s, 1H; Ar H), 7.89 (s, 2H; Ar H), 8.17 ppm (d, J = 8 Hz, 4H; Ar H); ¹³C NMR (400 MHz, $[D_8]$ THF): $\delta = 109.54$, 120.47, 123.81, 124.23, 126.12, 128.72, 140.43 ppm.

9,9'-(5-(Diethoxy(methyl)silyl)-1,3-phenylene)bis(9H-carbazole)

Under an argon atmosphere, chlorodiethoxy(methyl)silane (2.5 mL, 20 mmol) and magnesium powder (0.24 g, 10 mmol) were added in anhydrous THF (30 mL). The reaction flask was heated to 70 °C and a solution of 9,9'-(5-bromo-1,3-phenylene)bis(9*H*-carbazole) (4.87 g, 10 mmol) in THF (50 mL) was added drop-wise during 30 min. After the addition was completed, the mixture was stirred for 3 h at this temperature. The mixture was then cooled to room temperature and extracted with Et₂O. The solvent was evaporated in vacuo to give the crude product, which was purified by column chromatography on silica gel using (petroleum ether: dichloromethane = 6:1 v/v) as the eluent to obtain the product as a colourless

oil (3.46 g, 64%). ¹H NMR (400 MHz, $[D_8]$ THF): $\delta = 0.37$ (s, 3 H, -CH₃), 1.73 (t, J = 7 Hz, 6H; -OCH₂CH₃), 3.84 (q, J = 7 Hz, 4H; -OCH₂), 7.25 (t, J = 8 Hz, 4H; Ar H), 7.42 (t, 4H; Ar H), 7.56 (d, J = 8 Hz, 4H; Ar H), 7.95 (s, 1H; Ar H), 8.0 (s, 2H; Ar H), 8.14 ppm (d, J = 8 Hz, 4H; Ar H), 1³C NMR (400 MHz, $[D_8]$ THF): $\delta = -8.10$, 16.01, 56.62, 107.62, 118.23, 121.81, 124.06, 129.08, 137.22, 138.26, 138.84 ppm; ²⁹Si NMR (400 MHz, $[D_8]$ THF): $\delta = -22.17$ ppm; elemental analysis calcd for C₃₃H₃₂N₂O₂Si: C 77.74, H 5.96, N 5.18; found: C 77.78, H 5.91, N 5.20.

ODCzMSi

To a mixture of 9,9'-(5-(diethoxy(methyl)silyl)-1,3-phenylene)bis(9Hcarbazole) (1.08 g, 2 mmol) and THF (100 mL), water (2 mL) and 1 м HCl (2 drops) was added. The mixture was stirred at 0°C for 24 h. After the reaction was complete, the mixture was extracted with Et₂O and washed with distilled water three times and dried over anhydrous magnesium sulfate. The filtrate was concentrated by reduced pressure to give OH-Si monomer to which was added a solution of 9,9'-(5-(diethoxy(methyl)silyl)-1,3-phenylene)bis(9Hcarbazole) (1.08 g, 2.0 mmol) in THF (50 mL) and tetra-n-butyl titanate (2 drops) as catalyst. The mixture was stirred at 80°C for 5 days while tracking the progress of the reaction with a Fourier transform infrared (FTIR) spectrometer. After the reaction was complete, trimethylchlorosilane (0.5 mL) was added and stirred for another 12 h. Afterwards, the solvent was evaporated in vacuum to give a sticky liquid, which was dissolved in toluene and precipitated with methanol to obtain the product as white powder. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.02 - 7.52$ (m, 13H; ArH), 7.71-8.23 (m, 6H; ArH), 0.33 ppm (s, 3H; -CH₃); GPC (RI, polystyrene calibration) $Mw = 2.13 \times 10^3$, Mw/Mn = 1.13.

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Organic Electronics

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Oligosiloxane Functionalized with Pendant (1,3-Bis(9-carbazolyl)benzene) (mCP) for Solution-Processed Organic Electronics



Won't forget: Oligosiloxane (ODCzMSi) functionalized with mCP has been synthesized and shown to have outstanding properties for solution-processed electronics applications. The hybrid material has high thermal and morphological stability and high triplet energy. A phosphorescent OLED with an emissive layer of ODCzMSi–FIrpic shows very high efficiency blue emission. Efficient memory devices using ODCzMSi as the active layer have also been demonstrated.

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