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Conjugated Asymmetric Donor-Substituted 1,3,5-Triazines: New Host Materials for Blue Phosphorescent Organic Light-Emitting Diodes

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Abstract: Conjugated asymmetric donor-substituted 1,3,5-triazines (ADTs) have been synthesized by nucleophilic substitution of organolithium catalyzed by $[Pd(PPh_3)_4]$. Theoretical and experimental investigations show that ADTs possess high solubility and thermostability, high fluorescent quanyield (35%), low HOMO tum

(-6.0 eV) and LUMO (-2.8 eV), and high triplet energy ($E_{\rm T}$, 3.0 eV) according to the different substitution pattern

Keywords: asymmetric architectures · conjugation · donor-acceptor systems • organic light-emitting diodes • lithium • phosphorescence

of triazine. The application as host materials for blue PHOLEDs yielded a maximum current efficiency of 20.9 cd A⁻¹, a maximum external quantum efficiency of 9.8%, and a brightness of 9671 cd m⁻² at 5.4 V, making ADTs good candidates for optoelectronic devices.

Introduction

The fascination of donor-acceptor (D-A, or p-n) architectures^[1] has been widely recognized in the design of organic optoelectronic materials for organic light emitting diodes (OLED).^[2] organic photovoltaics (OPV).^[3] sensors.^[4] organic field-effect transistor (OFET),^[5] non-linear optics (NLO), magnetic materials,^[6] and many more.^[7] Plenty of organic donors have been developed for this design of functional materials due to the electron-rich feature of the π -conjugated systems.^[8] However, organic acceptors are quite few. Among the limited members of acceptors such as pervlene diimides,^[9] pyridines,^[10] pyrimidines,^[11] 1,3,4-oxadiazoles,^[12] 1,2,4-triazoles,^[13] and benzothiadiazoles,^[14] triazines have relatively high electron affinity and good thermal stability, which are very attractive for the D-A system design. The 2,4,6-tris(di-2-pyridylamino)-1,3,5-triazine and 2,4,6-tris(p-

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(di-2-pyridylamino) phenyl)-1,3,5-triazine were synthesized and used as blue-emitting materials.^[15] 2,4,6-Tris(diarylamino)-1,3,5-triazines^[16] and bitriazines derivatives^[17] were reported as electron-transport host materials for OLEDs. 2,4,6-Tris(carbazole)-1,3,5-triazine (TCzT) was found to be a highly efficient bipolar host material for phosphorescent OLEDs (PHOLEDs).^[18] Star-shaped 1,3,5-triazines with cyanovinylene 4-nitrophenyls arms were used for OPV with a power conversion efficiency of up to 3.82 %.^[19] In addition, the NLO properties of triazine derivatives based on 2,4,6tris(benzyloxy)-1,3,5-triazine were also published.^[20] These reported triazine derivatives with D-A architectures are mostly the octupolar symmetrical molecules. It is well known that asymmetric architectures could increase the number of the conformers and amount of energy for the crystallization, which favor the stability of amorphous film for high-performance devices.^[21] Strohriegl et al. reported a series of asymmetric triazine derivatives with a flexible linkage (C-O bond) between the triazine core and the donor moiety for blue PHOLEDs,^[22] and high glass transition temperature (up to 170°C) and triplet energy (up to 2.96 eV) of the material were also observed. In addition, asymmetric triazines with donors connected directly to the triazine core (acceptor) can benefit both from the D-A architectures and from the fine turning of the energy levels of the materials.^[23] However, there are limited studies on the conjugated asymmetric triazine derivatives for organic electronics, especially in the field of blue PHOLEDs. These considerations motivated us to design and investigate the conjugated asymmetric donor-substituted triazine derivatives, although it is difficult to prepare them.

In this manuscript, a series of conjugated asymmetric donor-substituted 1,3,5-triazines (ADTs) were successfully synthesized through catalytic nucleophilic substitution of organolithium with an innovative synthetic strategy

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(Scheme 1). The prepared ADTs have good solubility due to the asymmetric structures and high thermostability for device fabrications. The different photophysical properties of the D-A type ADTs were observed because of the different substitution pattern of the donors. ADTs can not only be good host materials for blue PHOLEDs with a high triplet

Table 1. Optical and thermal properties of the ADTs.

	$UV_{\lambda max}$ [nm]			PL	PL _{lmax} [nm]		$T_{\rm d}$	$\phi_{ m F}$
	CHCl ₃	film	$E_{\rm opt}$	CHCl ₃	film	[°C]	[°C]	film
TCzT ^[16]	_	289, 333	3.4	_	392, (425)	452	_	_
ThDCzT	278, 324	279, 328	3.32	452	452	266	439	0.061
PhDCzT	278, 326	282, 326	3.41	452	439	268	445	0.096
NPhDCzT	278, 311, 323	292, 314, 327	3.64	461	379, 398	> 300	450	0.351
DThCzT	277, 323	278, 331	3.22	480	454	246	365	0.076
DPhCzT	270, 322	278, 329	3.37	474	417, 441, 464	286	369	0.041
DNPhCzT	278, 307, 320	280, 310, 322	3.70	447	373, 393	290	422	0.348

energy up to 3.0 eV, but also blue-light-emitting materials with the quantum efficiency up to 35% in solid film (Table 1). These properties indicate that the ADTs have great potential for organic electronics, especially for blue PHOLEDs. To the best of our knowledge, this is the first conjugated asymmetric donor-substituted 1,3,5-triazines for blue PHOLEDs.

Results and Discussion

The structures and synthetic routes of ADTs are shown in Scheme 1. The ADTs were synthesized through nucleophilic substitution of the cyanuric chloride in two steps with high yields. In the first step, the mono- and diaryl (Ph, Th, and NPh)-substituted triazines were prepared by using a Grignard reaction and nucleophilic substitution, according



Scheme 1. Synthesis of the asymmetric donor-substituted 1,3,5-triazines (ADTs).

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to the different reactivity of chlorine of cyanuric chloride at different temperatures.^[24] In the second step (see Scheme 1), the catalyzed nucleophilic substitution of the cyanuric chlorine with lithium carbazole results in the desired compounds. Without the $[Pd(PPh_3)_4]$ catalyst, the yield is very low (around 25%). Another synthetic route with inversed synthesis sequence, that is, carbazole substitution followed by Grignard reaction, turns out to be unsuccessful, due to the poor reactivity of the dichorotriazine towards Grignard C–C coupling as illustrated in Scheme S1 in the Supporting Information. This successful and efficient synthetic route with the innovative Pd catalyzed nucleophilic substitution method makes the preparation of various donor-substituted carbazole-based 1,3,5-triazines feasible, which will greatly promote the research of the triazine-based materials.

The ADTs have good solubility in chloroform and chlorobenzene, which greatly improves the processability and applications of the triazine-based materials. The starting temperature of thermal decomposition (T_d) of the compounds is between 365 °C and 450 °C (see Table 1), and a high content of carbazoles results in a higher T_d . Their melting points (T_m) are all above 245 °C and no glass transition temperature was observed by differential scanning calorimetry (DSC). The thermal properties of ADTs are quite good for optoelectronic devices.

The normalized UV/Vis absorption and photoluminescent (PL) spectra of ADTs in both CHCl₃ solution and thin solid film were shown in Figure 1 and summarized in Table 1. Two absorption bands around 275 and 320 nm were observed for all the six ADTs both in solution and film, in which the band around 275 nm can be associated with $n-\pi^*$ transition,^[8a,25] and the other bands around 320 nm are as-



Figure 1. Normalized optical absorption and photoluminescent spectra of ADTs a) in dilute chloroform solution and b) in solid film.

signed to $\pi - \pi^*$ transition of the conjugated backbone. The optical energy band gaps (E_{opt}) of ADTs determined from the onset of UV/Vis spectra in solid film range from 3.22 to 3.70 eV with the corresponding order: DNPhCzT > NPhDCzT > PhDCzT > TCzT > DPhCzT > ThDCzT >

DThCzT. The ADTs exhibit blue emissions in chloroform and their PL peaks range from 447 to 480 nm according to the different substitution pattern of the 1,3,5-triazine. The absent PL data of TCzT in chloroform is due to its poor solubility in organic solutions. In the solid state, the PL spectra of ADTs are blueshifted up to 63 nm in comparison with that in solution, probably due to the better stabilizing effects of the solvent on the base state (S_0) than the excited state (S₁) of the D-A structure of ADTs.^[26] The strongest PL peaks of ThDCzT, PhDCzT, DThCzT, and DPhCzT in solid film are significantly redshifted with low photoluminescent efficiency (<10%) in comparison with that of NPhDCzT and DNPhCzT. The low quantum efficiency is probably due to the intermolecular aggregation because of the planar architectures as revealed by the DFT-optimized structures. The high quantum efficiency (approx. 35%) of NPhDCzT and DNPhCzT in film suggests they have a good potential as blue OLED emitters, which maybe attribute to nonplanar architectures of NPhDCzT and DNPhCzT.

From the HOMOs and LUMOs of ADTs shown in Figure 2, the LUMO has high distribution density on triazine core because it is an acceptor, whereas the HOMOs are dominated by the carbazole substituent because it is a strong donor. This D–A architecture of ADTs can lead to separated electron density distribution between the HOMO and LUMO, which is very obvious in ThDCzT, PhDCzT, DThCzT, and DPhCzT. This separation provides the material with a charge–transfer (C–T) state as observed in PL spectra, efficient hole- and electron-transporting properties, and the prevention of reverse energy-transfer, which enables the related ADTs to have excellent potential as host materials.^[27]

Electrochemical properties of ADTs were further investigated by cyclic voltammetry (CV). All the compounds underwent quasi-reversible redox behavior. From the onset potential of electrochemical reduction and oxidation, the LUMO, HOMO, and the energy gap (E_g) were calculated and listed in Table 2. Since the HOMOs of ADTs are dominated by carbazole (see Table 2), their energy levels of

Table 2. Experimental and theoretical HOMO, LUMO and triplet-state energy [eV] of ADTs.

	From CV			From calculation				$exptl}E_T$
	HOMO	LUMO	E_{g}	HOMO	LUMO	E_{g}	$^{calcd}E_{T}$	
TCzT	$-6.0^{[a]}$	$-2.6^{[a]}$	-	-5.80	-1.39	4.41	3.09	$2.81^{[a]}$
ThDCzT	-6.04	-2.82	3.22	-5.79	-1.96	3.83	2.62	2.94
PhDCzT	-6.06	-2.80	3.26	-5.80	-1.82	3.98	3.14	2.94
NPhDCzT	-5.99	-2.22	3.77	-5.64	-1.11	4.53	3.09	3.00
DThCzT	-6.04	-2.88	3.16	-5.79	-2.04	3.75	2.61	2.65
DPhCzT	-6.03	-2.81	3.22	-5.78	-1.91	3.87	3.10	2.96
DNPhCzT	-5.91	-1.98	3.93	-5.51	-0.80	4.70	3.10	2.97

[a] Measured by ultraviolet photoelectron spectroscopy, see ref. [16].

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Figure 2. The computed spatial distributions of HOMOs and LUMOs of ADTs.

HOMO are similar with little variation (< 0.1 eV), whereas for LUMOs, a significant difference was observed. This independent modification of HOMO and LUMO of ADTs with various substituents can greatly facilitate the molecular design of the desired materials. In comparison with TCzT, the substitution of diphenylamine leads to an increased LUMO, whereas the other substituents result in a decreased LUMO in the following order: DNPhCzT > NPhDCzT > TCzT > PhDCzT > DPhCzT > ThDCzT > DThCzT. This order also exists for E_g , because the HOMOs of ADTs are almost identical. The CV-measured frontier orbitals are well predicted by the DFT calculations with good coordination as listed in Table 2. The lower LUMOs of ADTs suggest properties such as good electron ejection and transportation of the material, which is very crucial for organic optoelectronic devices.

Phosphorescent spectra of ADTs were measured at 77 K with 5 ms delay as shown in Figure S1 in the Supporting Information. The triplet-state energy $(^{exptl}E_T)$ listed in Table 2 was obtained by taking the highest energy peak of phosphorescent spectra as the transition energy of $T_1 \rightarrow S_0$. Small systemic errors (<0.3 eV) between DFT calculations and experimental measurements on evaluating triplet-state (T_1) energy was observed with good coordination. With the exception of DThCzT (2.65 eV), ADTs show a higher $^{exptl}E_T$ (2.94–3.00 eV) than TCzT (2.81 eV), which is very good as host materials for blue PHOLEDs.^[28]

To further investigate the potential of ADTs for optoelectronic devices, ADTs and TCzT (used for comparison) were chosen to act as host materials for blue PHOLEDs. Iridium(III) [bis(4,6-difluorophenyl)-pyridinato-N,C²] picolinate (FIrpic), with two emission peaks (a typical emission peak around 472 nm and a shoulder at 500 nm) and the $E_{\rm T}$ of 2.62 eV,^[29] was used as guest material because it is one of the most efficient and popular blue phosphorescent dyes for OLED. The ADTs hosted PHOLEDs were fabricated with the device configuration: ITO/MoOx (2 nm)/m-MTDATA: MoOx (15 wt. %, 30 nm)/*m*-MTDATA (10 nm)/Ir(ppz)₃ (10 nm)/ADTs or TCzT:FIrpic (10 wt.%, 10 nm)/BPhen (40 nm)/LiF (1 nm)/Al. The electroluminescence (EL) spectra were shown in Figure 3 and the correlative properties were summarized in Table 3. The EL spectra of ADTs hosted devices resemble the PL spectrum of FIrpic^[29] and are more stable than that of TCzT with the increasing current density, which indicates that PhDCzT, NPhDCzT, and DNPhCzT are good host materials for blue PHOLEDs.^[30] In addition, lower turn-on voltages (below 2.8 V) and higher maximum external quantum efficiencies (EQE) of up to 9.8, 9.0, and 9.3% (see Table 3) were also observed. Excitedly, these three devices have high brightness (9671, 7771, and 4566 cd m^{-2} , respectively) at a low voltage of 5.4 V (see Figure 4). PhDCzT, NPhDCzT, and DNPhCzT-based devices show maximum current efficiency of 20.9, 17.4, and 18.3 cd A⁻¹ and maximum power efficiency of 21.0, 17.1, and

Table 3. Electroluminescent properties of ADTs as host materials for blue PHOLED.

Device	$\eta_{ m max} \ [m cdA^{-1}]^{[a]}$	$\eta_{ m max} \ [m lmW^{-1}]^{[b]}$	$V_{ ext{turn-on}}$ [V]	$B \ [cd m^{-2}]^{[c]}$	EQE _{max} [%]
TCzT	10.4	9.3	2.85	1263	5.2
PhDCzT	20.9	20.0	< 2.8	9671	9.8
NPhDCzT	17.4	17.1	$<\!2.8$	7771	9.0
DNPhCzT	18.3	17.9	< 2.8	4566	9.3

[a] Maximum current efficiency. [b] Maximum power efficiency. [c] Luminance at 5.4 V.



Figure 3. Normalized electroluminescence spectra of a) PhDCzT, b) NPhDCzT, c) DNPhCzT, and d) TCzT-based devices. Key: $\blacksquare = 10$; $\bullet = 20$; $\blacktriangle = 30$; $\blacktriangledown = 40$; $\triangleleft = 50 \text{ mA cm}^{-2}$.



Figure 4. Current efficiency–voltage–luminance characteristics of PhDCzT (\bullet), NPhDCzT (\bullet), DNPhCzT (\bullet), and TCzT-based (\checkmark) devices.

17.9 Lm W⁻¹, respectively. The symmetric TCzT-based device shows lower EQE of 5.2% and efficiencies of 10.4 cd A⁻¹ and 9.3 Lm W⁻¹ under the same device structure (see Table 3), which suggests that conjugated asymmetrical ADTs are better host materials for blue PHOLEDs.

Conclusion

In summary, a novel series of conjugated asymmetric donorsubstituted 1,3,5-triazines (ADTs) have been synthesized according to an innovative synthetic strategy that will greatly promote the research of the triazine-based D–A molecules. The prepared ADTs have good solubility and high thermostability for device fabrications. The typical D–A compounds of ThDCzT, PhDCzT, DThCzT, and DPhCzT with separated electron density distribution of frontier orbitals show low LUMO (-2.80 to -2.88 eV) and high $E_{\rm T}$ (2.65– 2.96 eV) as revealed by both theoretical and experimental investigations, indicating they are very good host materials for blue PHOLEDs. The devices show that the conjugated asymmetrical ADTs have lower turn-on voltage, higher efficiencies, and higher brightness and stability than the symmetrical TCzT as host materials for FIrpic. The conjugated ADTs are very interesting optoelectronic materials and their photophysical properties can be effectively modified by asymmetric donor substitution.

Experimental Section

Materials: All manipulations involving air-sensitive reagents were performed in an atmosphere of dry N_2 . Tetrahydrofuran (THF) and toluene were dried and purified by routine procedures. All reagents, unless otherwise specified, were purchased from Aldrich, Acros, or Alfa Aesar, and used without further treatments.

Measurements: NMR spectra were collected on a Bruker Ultra Shield Plus 400 MHz instruments with CDCl₃ and [D]DMSO as the solvent and tetramethylsilane (TMS) as the internal standard. GC-MS experiments were carried out using a Shimadzu GCMS-QP2010. MALDI-TOF-MS was determined on a Buker Daltonics flex Analysis. Elemental analyses were performed on Elementar Vario MICRO elemental analyzer. Mass spectrometric data were obtained on a LCT Premier XE (Waters) mass spectrometry and an ESI-TOF HRMS spectrometry. Thermogravimetric analyses (TGA) were conducted on a DTG-60 Shimadzu thermal analyst

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system under a heating rate of 10°Cmin⁻¹ and a nitrogen flow rate of 50 cm³min⁻¹. Differential scanning calorimetry (DSC) was run on a Pyris 1 DSC (Perkin Elmer Co.) thermal analyst system under a heating rate of 20°Cmin⁻¹ and an argon flow rate of 50 cm³min⁻¹. Ultraviolet/visible (UV/Vis) spectra were recorded on an UV-3600 SHIMADZU UV/Vis-NIR spectrophotometer and fluorescence spectra were obtained using a RF-5301PC spectrofluorophotometer with a xenon lamp as a light source. The concentrations of the compound solutions (in CHCl₃) were adjusted to about 0.01 mgmL⁻¹ or less. The thin solid films were prepared by casting solution of the compounds on quartz substrates. The phosphorescence spectra of the compounds (in CHCl₃) were measured using an Edinburgh LFS920 fluorescence spectrophotometer at 77 K, with a 5 ms delay time after the excitation (λ =337 nm) with a microsecond flash lamp. The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and the energy gap between them (E_g) were measured by cyclic voltammetry (CV). The CV measurements were performed at room temperature on a CHI660E system in a typical three-electrode cell with a working electrode (glass carbon), a reference electrode (Ag/Ag⁺, referenced against ferrocene/ferrocenium (FOC)), and a counter electrode (Pt wire) in an acetonitrile solution of Bu_4NPF_6 (0.10 M) at a sweeping rate of 100 mV s⁻¹. The HOMO/ LUMO energy levels of the material are estimated based on the reference energy level of ferrocene (4.8 eV below the vacuum): HOMO/ LUMO = $-[E_{onset}-(-0.017)]-4.8$ eV, in which the value of 0.017 V is for FOC versus Ag/Ag⁺ and E_{onset} is the onset potential of the oxidation or the reduction.

Computational methods: Theoretical calculations were performed on Gaussian 03 program with the Becke's three-parameter exchange functional along with the Lee Yang Parr's correlation functional (B3LYP) using 6–31G (d) basis sets. The ground and lowest triplet-state geometries were fully optimized and these optimized stationary points were further characterized by harmonic vibration frequency analysis to ensure that real local minima had been found. The properties of the designed model compounds in Table S1, such as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy, energy gap (E_g), and triplet-state energy (${}^{3}E_g$) were derived from the computed results according to literature publications.^[7d,26,31]

Device fabrication and measurement: In a general procedure, ITOcoated glass substrates were etched, patterned, and washed with detergent, deionized water, acetone, and ethanol in turn. Organic layers were deposited by high-vacuum ($\approx 4 \times 10^{-4}$ Pa) thermal evaporation with a rate of 0.1–0.2 nm s⁻¹. To reduce the ohmic loss, a layer heavily *p*-doped with MoO_x (because of the low doping efficiencies of transition-metaloxide-based acceptors in amorphous organic matrixes) was directly deposited onto the ITO substrate for each sample. The layer thickness and the deposition rate were monitored in situ by an oscillating quartz thickness monitor. The devices without encapsulation were measured immediately after fabrication under ambient atmosphere at room temperature. Electroluminescent (EL) spectra of the devices were measured by a PR650 spectroscan spectrometer. The luminance–voltage and current– voltage characteristics were measured simultaneously with a programmable Keithley 2400 voltage–current source.

Synthesis of monomer 2,4-dichloro-6-(thiophen-2-yl)-1,3,5-triazine: Procedure 1: A solution of 2-bromothiophene (2.12 g, 13.0 mmol) in dry THF (15 mL) was added slowly to a stirred mixture of magnesium turnings (0.34 g, 14.0 mmol) in dry THF (5 mL) containing a catalytic amount of iodine under nitrogen to obtain the Grignard reagent. The Grignard reagent solution was dropped slowly into a stirred solution of 2,4,6-trichloro-1,3,5-triazine (2.0 g, 10.8 mmol) in dry THF (20 mL) at 0 °C. After stirring for 4 h, the mixture was poured into water and extracted with CH₂Cl₂. The layers were separated, and the organic layers were collected and dried over sodium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by flash column chromatography to give a yellow solid (0.9 g, 36% yield). GC-MS (CH₂Cl₂) *m/z*: 231. ¹H NMR (CDCl₃, 400 MHz): δ =129.29, 135.09, 136.17, 137.97, 170.19, 171.61 ppm.

2-Chloro-4,6-di(thiophen-2-yl)-1,3,5-triazine: Following the above procedure 1, 2.9 g (65% yield) of yellow solid was obtained from 2-bromothiophene (3.89 g, 23.9 mmol), magnesium turnings (0.61 g, 24.9 mmol), and 2,4,6-trichloro-1,3,5-triazine (2.0 g, 10.8 mmol) at 35 °C for 12 h. GC-MS (CH₂Cl₂): m/z: 279. ¹H NMR (CDCl₃, 400 MHz): δ =8.26 (d, 2H), 7.69 (d, 2H), 7.22 ppm (t, 2H).

2,4-Dichloro-6-phenyl-1,3,5-triazine: Following the above standard procedure 1, 1.16 g (47% yield) of white solid was obtained from bromobenzene (1.36 mL, 13.0 mmol), magnesium turnings (0.34 g, 14.0 mmol), 2,4,6-trichloro-1,3,5-triazine (2.0 g, 10.8 mmol) at 0 °C for 4 h. GC-MS (CH₂Cl₂): m/z: 225.

2-Chloro-4,6-diphenyl-1,3,5-triazine: Following the above standard procedure 1, 2.18 g (50 % yield) of white solid was obtained from bromobenzene (8.7 g, 55.4 mmol), magnesium turnings (1.38 g, 57.5 mmol), 2,4,6-trichloro-1,3,5-triazine (3.0 g, 16.2 mmol) at 35 °C for 12 h. GC-MS (CH₂Cl₂): *m/z*: 267; ¹H NMR (CDCl₃, 400 MHz): δ =8.59 (d, 4H), 7.61 (t, 2H), 7.52 ppm (t, 4H); ¹³C NMR (CDCl₃, 100 MHz): δ =173.36, 172.17, 134.35, 133.56, 129.40, 128.82 ppm.

Synthesis of monomer 4,6-dichloro-2-(*N*,*N*-diphenyl)-1,3,5-triazine: Procedure 2: Diphenylamine (2.02 g, 12.0 mmol) was placed in a 50 mL round-bottom flask equipped with a stir. Dry THF (20 mL) was injected with a syringe into the flask under nitrogen atmosphere. Then the solution was cooled in an icy bath and stirred for ten minutes. Then, 1.6 m butyllithium/hexane solution (8.1 mL, 13.0 mmol) was added slowly into the solution. The mixture was stirred for another 30 min at room temperature, and its color became yellow. Then, the yellow solution was slowly dropped into a stirred solution of 2,4,6-trichloro-1,3,5-triazine (2.0 g, 10.8 mmol) in dry THF (20 mL) at 0°C for 30 min. After stirring for 4 h at 0°C, the mixture was poured into water and extracted with CH₂Cl₂. The layers were separated, and the organic layers were collected and dried over sodium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by flash column chromatography to give a yellow solid (3.0 g, 87% yield). GC-MS (CH₂Cl₂): *m/z*: 315.

6-Chloro-2,4-di(*N*,*N*-**diphenyl)-1,3,5-triazine**: Following the standard procedure 2, 0.87 g (74% yield) of yellow solid was obtained from diphenylamine (0.96 g, 5.67 mmol), 1.6 *м n*-butyllithium/hexane solution (3.7 mL, 5.96 mmol), and 2,4,6-trichloro-1,3,5-triazine (0.5 g, 2.71 mmol) at 35 °C for 12 h. GC-MS (CH₂Cl₂): *m/z*: 448; ¹H NMR (CDCl₃, 400 MHz): δ = 7.25 (t, 8H), 7.17–7.11 ppm (m, 12H). ¹³C NMR (CDCl₃, 100 MHz): δ = 169.90, 165.61, 142.63, 128.77, 127.47, 126.15 ppm.

Synthesis of 9,9'-[6-(thiophen-2-yl)-1,3,5-triazine-2,4-diyl]bis(9H-carbazole) (ThDCzT): Procedure 3: 9H-carbazole (0.5 g, 3.0 mmol) was placed in a 50 mL round-bottom flask equipped with a stir. Dry THF (5 mL) was injected with a syringe into the flask under nitrogen atmosphere. Then the solution was cooled in an icy bath and stirred for ten minutes, and 1.6 M n-butyllithium/hexane solution (1.94 mL, 3.1 mmol) was added into slowly. The mixture was stirred for another 30 min at room temperature to form yellow slurry. A mixture of 2,4-dichloro-6-(thiophen-2-yl)-1,3,5-triazine (0.3 g, 1.3 mmol) and [Pd(PPh₃)₄] (160 mg, 0.13 mmol) in THF (5 mL) were slowly dropped into the slurry of the prepared lithium carbazole. A large amount of solid product was precipitated. The mixture was heated at 80°C overnight. The precipitation was filtered and washed with water and acetone several times. The solid was first dried in air and then recrystallizations from chlorbenzene to give a solid (0.46 g, 72%). ¹H NMR (CDCl₃, 400 MHz): $\delta = 9.04$ (d, 4 H), 8.42 (s, 1 H), 8.10 (d, 4 H), 7.75 (s, 1H), 7.54 (t, 4H), 7.44 (t, 4H), 7.34 ppm (d, 1H); ¹³C NMR $(CDCl_3, 100 \text{ MHz}): \delta = 168.56, 164.40, 141.85, 138.91, 132.52, 131.80,$ 128.74, 126.99, 126.60, 123.40, 119.68, 117.72 ppm; MALDI-TOF: m/z calcd for $C_{31}H_{19}N_5S$: 493.58 $[M+H]^+$; found: 494.379; elemental analysis calcd (%) for $C_{31}H_{19}N_5S$: C 75.43, H 3.88, N 14.19, S 6.50; found: C 75.46, H 3.81, N 13.94.

9-[4,6-Di(thiophen-2-yl)-1,3,5-triazin-2-yl]-9*H***-carbazole (DThCzT): Following procedure 3, 0.22 g (50 % yield) of target product was obtained from 9***H***-carbazole (0.22 g, 1.3 mmol), 1.6 \mu** *n***-butyllithium/hexane solution (0.87 mL, 1.3 mmol), 2-chloro-4,6-di(thiophen-2-yl)-1,3,5-triazine (0.3 g, 1.1 mmol) and [Pd(PPh₃)₄] (140 mg, 0.11 mmol) at 80 °C for 12 h. ¹H NMR (CDCl₃, 400 MHz): 9.17 (d, 2H); 8.37 (d, 2H); 8.08 (d, 2H); 7.71 (d, 2H); 7.61 (t, 2H); 7.45 (t, 2H); 7.30 ppm (t, 2H); ¹³C NMR**

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(CDCl₃, 100 MHz): δ =118.23, 119.54, 123.38, 126.76, 127.03, 128.56, 131.73, 132.30, 139.06, 141.76, 164.37, 168.15 ppm; HRMS (EI): *m/z* calcd for C₂₃H₁₄N₄S₂: 411.0738 [*M*+H]⁺; found: 411.0739.

9,9'-(6-Phenyl-1,3,5-triazine-2,4-diyl)bis(9*H***-carbazole) (PhDCzT): Following procedure 3, 0.38 g (58 % yield) of target product was obtained from 9H-carbazole (0.51 g, 3.1 mmol), 1.6** *m**n***-butyllithium/hexane solution (2.1 mL, 3.2 mmol), 2,4-dichloro-6-phenyl-1,3,5-triazine (0.3 g, 1.3 mmol) and [Pd(PPh_3)_4] (170 mg) at 80 °C for 12 h. ¹H NMR (CDCl₃, 400 MHz): \delta=9.05 (d, 4H), 8.76 (d, 2H), 8.11 (d, 4H), 7.69 (d, 2H), 7.57–7.44 ppm (m, 9H). ¹³C NMR (CDCl₃, 100 MHz): \delta=173.08, 164.78, 138.95, 136.20, 132.93, 129.23, 129.00, 127.02, 126.58, 123.38, 119.73, 117.56 ppm; MALDI-TOF:** *m/z* **calcd for C₃₃H₂₁N₅: 487.55 [***M***+H]⁺; found: 488.388; elemental analysis calcd (%) for C₃₃H₂₁N₅: C 81.29, H 4.34, N 14.36; found: C 80.92, H 4.39, N 14.39.**

9-(4,6-Diphenyl-1,3,5-triazin-2-yl)-9*H***-carbazole (DPhCzT)**: Following procedure 3, 0.2 g target product (65 % yield) was obtained from 9*H*-carbazole (0.15 g, 0.90 mmol), 1.6 м *n*-butyllithium/hexane solution (0.56 mL, 0.90 mmol), 2-chloro-4,6-diphenyl-1,3,5-triazine (0.2 g, 0.75 mmol) and [Pd(PPh₃)₄] (93 mg) at 80 °C for 12 h. ¹H NMR (CDCl₃, 400 MHz): $\delta =$ 9.17 (d, 2H); 8.78 (t, 4H); 8.10 (d, 2H); 7.66–7.60 (m, 8H); 7.45 ppm (t, 2H); ¹³C NMR (CDCl₃, 100 MHz): $\delta =$ 172.51, 165.26, 139.17, 136.31, 132.73, 129.16, 128.84, 127.03, 126.69, 123.31, 119.69, 117.74 ppm; MALDI-TOF: *m*/*z* calcd for C₂₇H₁₈N₄: 398.46 [*M*+H]⁺; found: 399.391; elemental analysis calcd (%) for C₂₇H₁₈N₄: C 81.39, H 4.55, N 14.06; found: C 81.43, H 4.78, N 13.77.

4,6-Di(9H-carbazol-9-yl)-N,N-diphenyl-1,3,5-triazin-2-amine

(**NPhDCzT**): Following procedure 3, 0.20 g (78 % yield) of target product was obtained from 9*H*-carbazole (0.23 g, 1.39 mmol), 1.6 м *n*-butyllithium/hexane solution (0.91 mL, 1.45 mmol), 4,6-dichloro-2-(*N*,*N*-diphenyl)-1,3,5-triazine (0.2 g, 0.63 mmol) and [Pd(PPh₃)₄] (93 mg) at 80 °C for 12 h. ¹H NMR (CDCl₃, 400 MHz): δ = 8.56 (d, 4H), 8.00 (d, 4H), 7.62–7.54 (m, 8H), 7.45 (t, 2H), 7.33 (t, 4H), 7.26 ppm (t, 4H); ¹³C NMR (CDCl₃, 100 MHz): δ = 167.01, 164.33, 143.18, 139.00, 129.62, 128.53, 127.12, 126.52, 126.28, 122.84, 119.34, 117.98 ppm; MALDI-TOF: *m/z* calcd for C₃₉H₂₆N₆, 578.66 [*M*+H]⁺; found 579.531; elemental analysis calcd (%) for C₃₉H₂₆N₆: C 80.95, H 4.53, N 14.52; found: C 80.65, H 4.58, N 14.41.

6-(9*H***-Carbazol-9-yl)-***N***2,***N***2,***N***4,***N***4-tetraphenyl-1,3,5-triazine-2,4-diamine (DNPhCzT**): Following procedure 3, 0.48 g (75 % yield) of target product was obtained from 9*H*-carbazole (0.22 g, 1.32 mmol), 1.6 *m n*-butyllithi-um/hexane solution (0.91 mL, 1.45 mmol), 6-chloro-2,4-di(*N*,*N*-diphenyl)-1,3,5-triazine (0.5 g, 1.11 mmol) and [Pd(PPh₃)₄] (93 mg, 0.074 mmol) at 80 °C for 12 h. ¹H NMR ([D]DMSO, 400 MHz): δ =8.00 (d, 2H, *J*=7.6 Hz), 7.74 (d, 2H, *J*=8.4 Hz), 7.68–6.94 (m, 22 H), 6.88 ppm (d, 2H, *J*=1.6 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ =166.49, 164.02, 143.39, 139.09, 128.99, 128.22, 128.00, 127.51, 126.09, 122.28, 118.83, 118.52 ppm; MALDI-TOF: *m*/*z* calcd for C₃₉H₂₈N₆: 580.68 [*M*+H]⁺; found 581.583; elemental analysis calcd (%) for C₃₉H₂₈N₆: C 80.67, H 4.86, N 14.47; found: C 80.54, H 4.88, N 14.44.

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[2] A. C. Arias, J. D. MacKenzie, I. McCulloch, J. Rivnay, A. Salleo, *Chem. Rev.* 2010, 110, 3–24.

- [3] a) S. Günes, H. Neugebauer, N. S. Sariciftci, *Chem. Rev.* 2007, 107, 1324–1338; b) K. Colladet, S. Fourier, T. J. Cleij, L. Lutsen, J. Gelan, D. Vanderzande, L. H. Nguyen, H. Neugebauer, S. Sariciftci, A. Aguirre, G. Janssen, E. Goovaerts, *Macromolecules* 2007, 40, 65–72; c) E. Bundgaard, F. C. Krebs, *Sol. Energy Mater. Sol. Cells* 2007, 91, 954–985; d) Y. J. Cheng, S. H. Yang, C. S. Hsu, *Chem. Rev.* 2009, 109, 5868–5923.
- [4] F. Jakle, Chem. Rev. 2010, 110, 3985-4022.
- [5] M. M. Durban, P. D. Kazarinoff, C. K. Luscombe, *Macromolecules* 2010, 43, 6348–6352.
- [6] T. D. Selby, K. R. Stickley, S. C. Blackstock, Org. Lett. 2000, 2, 171– 174.
- [7] a) W. L. Yu, H. Meng, J. Pei, W. Huang, Y. F. Li, A. J. Heeger, Macromolecules 1998, 31, 4838-4844; b) W. Huang, H. Meng, W. L. Yu, J. Pei, Z. K. Chen, Y. H. Lai, Macromolecules 1999, 32, 118-126; c) Y. Sakamoto, T. Suzuki, M. Kobayashi, Y. Gao, Y. Fukai, Y. Inoue, F. Sato, S. Tokito, J. Am. Chem. Soc. 2004, 126, 8138-8140; d) R. F. Chen, J. F. Pan, J. H. Pan, Y. Zhang, Q. L. Fan, W. Huang, J. Phys. Chem. A 2006, 110, 23750-23755; e) H. Y. Wang, J. H. Wan, H. J. Jiang, G. A. Wen, J. C. Feng, Z. J. Zhang, B. O. Peng, W. Huang, W. Wei, J. Polym. Sci. Part A: Polym. Chem. 2007, 45, 1066-1073.
- [8] a) S. L. Zhang, R. F. Chen, J. Yin, F. Liu, H. J. Jiang, N. E. Shi, Z. F. An, C. Ma, B. Liu, W. Huang, *Org. Lett.* **2010**, *12*, 3438–3441;
 b) Z. F. An, J. Yin, N. E. Shi, H. J. Jiang, R. F. Chen, H. F. Shi, W. Huang, *J. Polym. Sci. Polym. Chem. Ed.* **2010**, *48*, 3868–3879.
- M. Gsanger, J. H. Oh, M. Konemann, H. W. Hoffken, A. M. Krause,
 Z. N. Bao, F. Wurthner, *Angew. Chem.* 2010, 122, 752–755; *Angew. Chem. Int. Ed.* 2010, 49, 740–743.
- [10] N. Li, P. F. Wang, S. L. Lai, W. M. Liu, C. S. Lee, S. T. Lee, Z. T. Liu, *Adv. Mater.* 2010, 22, 527–530.
- [11] a) K. T. Wong, T. S. Hung, Y. T. Lin, C. C. Wu, G. H. Lee, S. M. Peng, C. H. Chou, Y. L. Su, *Org. Lett.* **2002**, *4*, 513–516; b) S. Achelle, Y. Ramondenc, F. Marsais, N. Ple, *Eur. J. Org. Chem.* **2008**, 3129–3140.
- [12] a) Y. Xin, G. A. Wen, W. J. Zeng, L. Zhao, X. R. Zhu, Q. L. Fan, J. C. Feng, L. H. Wang, W. Wei, B. Peng, Y. Cao, W. Huang, *Macro-molecules* **2005**, *38*, 6755–6758; b) R. Zhu, G. A. Wen, J. C. Feng, R. F. Chen, L. Zhao, H. P. Yao, Q. L. Fan, W. Wei, B. Peng, W. Huang, *Macromol. Rapid Commun.* **2005**, *26*, 1729–1735.
- [13] a) M. Mydlak, C. Bizzarri, D. Hartmann, W. Sarfert, G. Schmid, C. L. De, *Adv. Funct. Mater.* **2010**, *20*, 1812–1820; b) M. K. Kim, J. Kwon, T. H. Kwon, J. I. Hong, *New J. Chem.* **2010**, *34*, 1317–1322.
- [14] a) L. J. Huo, J. H. Hou, S. Q. Zhang, H. Y. Chen, Y. Yang, Angew. Chem. 2010, 122, 1542–1545; Angew. Chem. Int. Ed. 2010, 49, 1500– 1503; b) P. Sonar, S. P. Singh, S. Sudhakar, A. Dodabalapur, A. Sellinger, Chem. Mater. 2008, 20, 3184–3190.
- [15] J. Pang, Y. Tao, S. Freiberg, X. P. Yang, I. M. D, S. N. Wang, J. Mater. Chem. 2002, 12, 206–212.
- [16] H. Inomata, K. Goushi, T. Masuko, T. Konno, T. Imai, H. Sasabe, J. J. Brown, C. Adachi, *Chem. Mater.* 2004, *16*, 1285–1291.
- [17] H. L. Zhong, E. J. Xu, D. L. Zeng, J. P. Du, J. Sun, S. J. Ren, B. Jiang, Q. Fang, Org. Lett. 2008, 10, 709–712.
- [18] K. S. Son, M. Yahiro, T. Imai, H. Yoshizaki, C. Adachi, *Chem. Mater.* 2008, 20, 4439–4446.
- [19] J. A. Mikroyannidis, S. S. Sharma, Y. K. Vijay, G. D. Sharma, ACS Appl. Mater. Interfaces 2010, 2, 270–278.
- [20] K. Srinivas, S. Sitha, V. J. Rao, K. Bhanuprakash, K. Ravikumar, J. Mater. Chem. 2006, 16, 496–504.
- [21] a) P. Strohriegl, J. V. Grazulevicius, Adv. Mater. 2002, 14, 1439–1453; b) B. E. Koene, D. E. Loy, M. E. Thompson, Chem. Mater. 1998, 10, 2235–2250.
- [22] M. M. Rothmann, S. Haneder, C. E. Da, C. Lennartz, C. Schildknecht, P. Strohriegl, *Chem. Mater.* 2010, 22, 2403–2410.
- [23] A. J. Heeger, Chem. Soc. Rev. 2010, 39, 2354-2371.
- [24] M. B. Steffensen, E. Hollink, F. Kuschel, M. Bauer, E. E. Simanek, J. Polym. Sci. Polym. Chem. Ed. 2006, 44, 3411-3433.
- [25] a) Z. Q. Gao, M. Luo, X. H. Sun, H. L. Tam, M. S. Wong, B. X. Mi, P. F. Xia, K. W. Cheah, C. H. Chen, *Adv. Mater.* **2009**, *21*, 688–692;

a) W. L. Yu, H. Meng, J. Pei, W. Huang, J. Am. Chem. Soc. 1998, 120, 11808–11809; b) E. E. Havinga, H. W. Ten, H. Wynberg, Synth. Met. 1993, 55, 299–306.

CHEMISTRY

b) J. Y. Shen, X. L. Yang, T. H. Huang, J. T. Lin, T. H. Ke, L. Y. Chen, C. C. Wu, M. C. Yeh, *Adv. Funct. Mater.* 2007, *17*, 983–995;
c) S. Tang, M. Liu, P. Lu, H. Xia, M. Li, Z. Q. Xie, T. Z. Shen, C. Gu, H. P. Wang, B. Yang, Y. G. Ma, *Adv. Funct. Mater.* 2007, *17*, 2869–2877.

- [26] J. Yin, R. F. Chen, S. L. Zhang, Q. D. Ling, W. Huang, J. Phys. Chem. A 2010, 114, 3655–3667.
- [27] a) J. L. Brédas, D. Beljonne, V. Coropceanu, J. Chem. Rev. 2004, 104, 4971–5003; b) G. Qian, B. Dai, M. Luo, D. B. Yu, J. Zhan, Z. Q. Zhang, D. G. Ma, Z. Y. Wang, Chem. Mater. 2008, 20, 6208– 6216.
- [28] a) H. H. Chou, C. H. Cheng, Adv. Mater. 2010, 22, 2468–2471;
 b) S. O. Jeon, K. S. Yook, C. W. Joo, J. Y. Lee, Adv. Mater. 2010, 22, 1872–1876.
- [29] a) F. M. Hsu, C. H. Chien, C. F. Shu, C. H. Lai, C. C. Hsieh, K. W. Wang, P. T. Chou, *Adv. Funct. Mater.* **2009**, *19*, 2834–2843; b) S. H. Ye, Y. Q. Liu, J. M. Chen, K. Lu, W. P. Wu, C. Y. Du, Y. Liu, T. Wu, Z. G. Shuai, G. Yu, *Adv. Mater.* **2010**, *22*, 4167–4171.
- [30] S. H. Ye, Y. Q. Liu, C. A. Di, H. X. Xi, W. P. Wu, Y. G. Wen, K. Lu, C. Y. Du, Y. Liu, G. Yu, *Chem. Mater.* 2009, *21*, 1333–1342.
- [31] a) R. F. Chen, C. Zheng, Q. L. Fan, W. Huang, J. Comput. Chem.
 2007, 28, 2091–2101; b) L. Y. Zou, A. M. Ren, J. K. Feng, Y. L. Liu, X. Q. Ran, C. C. Sun, J. Phys. Chem. A 2008, 112, 12172–12178.

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