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# Synthesis, structures and charge—transfer complexations of 1,*n*-di-[3,6-di-(9-carbazolyl)-9-carbazolyl]alkanes with tetracyanoethylene and tetranitromethane

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# ABSTRACT

Synthesis and charge–transfer (CT) complexations of amorphous 3,6-di-(9-carbazolyl)-9-ethylcarbazole, 3,6-di-(9-carbazolyl)-9-ethylcarbazole and a series of 1,*n*-di-[3,6-di-(9-carbazolyl)-9-carbazolyl]alkanes (n = 1–5) with electron acceptors tetracyanoethylene and tetranitromethane are reported. The molar extinction coefficients ( $\varepsilon$ ), equilibrium constants ( $K_{eq}$ ), enthalpies ( $\Delta H$ ) and entropies ( $\Delta S$ ) of complexations have been determined. The low  $K_{eq}$  values (1.83–3.82 M<sup>-1</sup> for carbazole–TCNE and 0.28–0.45 M<sup>-1</sup> for carbazole–TNM complexes) show weak donor–acceptor associations. The negative values of  $\Delta H$  determined to be between  $-2.09 \pm 0.08$  and  $-3.10 \pm 0.21$  kcal mol<sup>-1</sup> for carbazole–TCNE complexes and  $-0.91 \pm 0.08$  and  $-3.31 \pm 0.28$  kcal mol<sup>-1</sup> for carbazole–TNM complexes indicate that complexations are driven by the exothermic enthalpies. Computational analysis using semi–empirical and DFT methods were applied to clarify the structures of the synthesized molecules and the nature of their CT complexations.

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# 1. Introduction

Amorphous molecular materials have been a subject of interest because of their glass-transition properties leading to forming thin films to be used in organic electroluminescent (EL) devices [1-3]. Besides their good thin film forming ability, amorphous molecular materials are also required to have high charge-carrier mobility in order to potentially be used in EL devices. Aromatic rings with  $\pi$ -electron system are included in the molecule to provide good charge-transporting property to the molecule. Examples of such molecules include derivatives of biphenyl, triphenylamine, arylhydrazone, anthracene, and carbazole [4-6]. Grigalevicius et al. and Kimoto et al. synthesized several 3,6-dicarbazolylcarbazole containing amorphous molecules and determined the thermal and optoelectronic properties of their thin films [7,8]. Since most of the both polymeric and molecular amorphous materials absorb light only in the UV region, usually their complexes or reaction products with various electron acceptors such as 2,4,7trinitrofluorenone (TNF), tetracyanoethylene (TCNE), and tetracvanoquinodimethane (TCNQ) are used in opto-electronic devices

http://dx.doi.org/10.1016/j.molstruc.2016.07.068 0022-2860/© 2016 Elsevier B.V. All rights reserved. to promote charge-generation in the visible region of the light spectra [9]. According to the molecular orbital theory, colored CT complex formation is due to electronic transition among highest occupied molecular orbitals (HOMOs) of the donor molecule to the lowest unoccupied molecular orbital (LUMO) of the acceptor. This usually results in more than one CT bands and can easily be diagnosed from their absorption spectra. Studies on charge-transfer complexation of a number of conjugated  $\pi$ -systems as electron donors with various electron acceptor molecules have already been performed and their results have been reported in the literature [10–14]. This paper deals with synthesis, structures and CT complexations of amorphous 3,6-di-(9-carbazolyl)-9-ethylcarbazole, 3,6-di-(9-carbazolyl)-9-hexylcarbazole and series of a series of 1,ndi-[3,6-di-(9-carbazolyl)-9-carbazolyl]alkanes (n = 1-5) with two of the electron acceptors, TCNE and TNM. For this purpose the equilibrium constant ( $K_{eq}$ ) and thermodynamic constants, enthalpy  $(\Delta H)$  and entropy changes  $(\Delta S)$ , of CT formations with TCNE and TNM in dichloromethane are investigated.

# 2. Experimental

# 2.1. Instrumentation

Absorbance measurements were recorded on a PG Instruments







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T80 + double beam UV–Visible spectrophotometer in 3.5 ml, 1.0 cm path length optical quartz cells with polytetrafluoroethylene (PTFE) stoppers using dichloromethane as the solvent. In the thermodynamic experiments a PTC–2 peltier temperature controller unit was attached to the UV–Vis spectrophotometer with a  $\pm$ 0.1 °C uncertainty of temperature. IR spectra were taken on a Perkin Elmer Spectrum Two FT–IR spectrometer using attenuated total reflection (ATR) sampling. <sup>1</sup>H and <sup>13</sup>C NMR data were obtained from an Agilent Technologies 400 MHz NMR spectrometer (in CDCl<sub>3</sub>, TMS as the internal reference). Thermal analyses (TGA and DSC) were carried out using a Setaram SETSYS Evolution TGA–DTA/DSC instrument.

#### 2.2. Materials

Carbazole and 9-ethylcarbazole were in 95–98 purity as received and purified via recrystallization from proper solvents prior to using. 1-Bromoheksane, dibromomethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane and ethylene di(p-toluenesulfonate) were purchased from global suppliers and used as received. The acceptors TCNE (Aldrich) was purified by sublimation and TNM was synthesized as described in the literature [15], purified by freeze–thaw method. CH<sub>2</sub>Cl<sub>2</sub> used in spectroscopic measurements were of analytical grade and used without further purification.

## 2.3. Synthesis

3,6-Diiodocarbazoles were achieved by a literature procedure using KI and KIO<sub>3</sub> in glacial acetic acid [16].

General procedure for the synthesis of 9-hexyl-3,6-diiodocarbazole (**4b**) and 1,n-di(3,6-diiodocarbazole-9-yl)alkanes (**6a**-**6e**): In a 100 ml round-bottom flask 4.19 g (10.0 mmol) of 1,3diiodocarbazole (**3**) was dissolved in 50 ml of dimethyl sulfoxide (DMSO) and 1,12 g (20.0 mmol) of KOH was added. The mixture was stirred for 30 min at room temperature to generate carbazolide anion. To this 5.0 mmol of the substrate molecule (1-bromohexane for **4b**, 1,n-dibromoalkane for **6a**, **6c**-**6e**, and ethylene di(ptoluenesulfonate) for **6b**) was added and the temperature was raised to 85–90 °C. After stirring at this temperature for 12 h, during which time a white precipitate evolved, the mixture was cooled to room temperature, filtered, washed first with water and then with ethanol to remove unreacted **3**, and air dried. The compounds **4b** and **6a**-**6e** were obtained as white powder and used in the next step without further treatment.

Synthesis of 9-ethyl-3,6-di-(9-carbazolyl)carbazole (5a): 1.25 g (7.5 mmol) of carbazole (1), 1.27 g (20 mmol) of Cu turnings, 5.0 g (36.2 mmol) of K<sub>2</sub>CO<sub>3</sub> and 0.26 g (1.0 mmol) of 18-crown-6 in 20 ml 1,2-dichlorobenzene were heated to reflux. Over one hour period, 2.24 g (5.0 mmol) of 9-ethyl-3,6-diiodocarbazole (4a) was added portion wise to the reaction mixture and further refluxed for 24 h. The organic component was separated trough filtration while hot and precipitated into 100 ml of methanol. The crude product was further purified via column chromatography (silica gel 60, 70-230 mesh) with dichloromethane/n-hexane (v/v [1/1]) as eluent. Yield: 1.65 g (63%) of a white powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.23$ (d, J = 1.77 Hz, 2H, ArH), 8.16 (d, J = 7.7 Hz, 4H, ArH), 7.7–7.6 (m, 4H, ArH), 7.40–7.24 (m, 12H, ArH), 4.58 (q, J = 7,2 Hz, 2H), 1.64 (t, J = 7.2, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 141.9; 139.7, 129.4, 126.0, 125.8, 123.5, 123.1, 120.2, 119.9, 119.6, 109.9, 109.7, 38.2, 14.1. FTIR (ATR) v (cm<sup>-1</sup>): 3050, 2975, 1626, 1594, 1573, 1496, 1478, 1451, 1335, 1318, 1294, 1275, 1232, 816, 806, 749, 723, 684, 653, 641, 620, 560. UV–Vis, [CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{max}$  (nm), ( $\varepsilon$ )]: 264 (6.78 × 10<sup>4</sup>), 294 (5.70 × 10<sup>4</sup>),  $342 (1.56 \times 10^4).$ 

Synthesis of 9-hexyl-3,6-di-(9-carbazolyl)carbazole (5b): The

compound **5b** was synthesized via the same procedure as **5a** from 1.01 g (2.0 mmol) of 3,6-diiodo-9-hexylcarbazole (4b), 1.0 g (6.0 mmol) of carbazole, 0.64 g (10.0 mmol) of Cu turnings and 2.37 g (17 mmol) of K<sub>2</sub>CO<sub>3</sub>. The crude product was purified via column chromatography (silica gel 60, 70-230 mesh) with dichloromethane/n-hexane (v/v [1/2]) as eluent. Yield: 0.68 g (59%) of a white powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.22$  (d, I = 1.59 Hz, 2H, ArH), 8.16 (d, I = 7.7 Hz, 4H, ArH), 7.68–7.66 (m, 4H, ArH), 7.40–7.24 (m, 12H, ArH), 4.49 (t, J = 7,4 Hz, 2H), 2.06 (quinted, J = 7.3 Hz, 2H), 1,60–1.34 (m, 6H), 0.94 (t, J = 7.2, 3H). <sup>13</sup>C NMR  $(100 \text{ MHz}, \text{CDCl}_3)$ :  $\delta = 141.9, 140.2, 129.3, 125.9, 125.8, 123.4, 123.1,$ 120.2, 119.8, 119.6, 110.1, 109.7, 43.7, 31.6, 29.1, 27.1, 22.6, 14.0. FTIR (ATR) v (cm<sup>-1</sup>): 3049, 2953, 2929, 2864, 1626, 1595, 1574, 1495, 1477, 1450, 1336, 1315, 1288, 1231, 807, 748, 724, 653, 641, 560. UV–Vis, [CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{max}$  (nm), ( $\varepsilon$ )]: 264 (5.76  $\times$  10<sup>4</sup>), 294 (5.10  $\times$  10<sup>4</sup>),  $343 (1.32 \times 10^4).$ 

Synthesis of 1,n-di-[3,6-di-(9-carbazolyl)-9-carbazolyl]alkanes (**7a**-**7e**): The compounds **7a**-**7e** were synthesized by the similar procedure as **5a** from 1.0 mmol of 1,n-di(3,6-diiodocarbazole-9-yl) alkane (n = 1-5, compounds **6a**-**6e**), 1.0 g (6.0 mmol) of carbazole, 0.64 g (10.0 mmol) of Cu turnings and 2.37 g (17 mmol) of K<sub>2</sub>CO<sub>3</sub>. The crude products were purified via column chromatography (silica gel 60, 70–230 mesh) with dichloromethane/n-hexane (v/v [1/2]) as eluent.

*Di*-[3,6-*di*-(9-*carbazolyl*)-9-*carbazolyl*]*methane* (**7a**). Yield 0.720 g (71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.32 (d, *J* = 1.9 Hz, 4H, ArH), 8.16 (d, *J* = 7.8 Hz, 8H, ArH), 7.92 (d, *J* = 8.6 Hz, 4H, ArH), 7.76 (dd, *J* = 8.6, 2.4 Hz, 4H, ArH), 7.41–7.38 (m, 16H, ArH), 7.31–7.26 (m, 8H, ArH), 7.08 (s, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 141.6, 139.8, 131.1, 126.8, 126.0, 124.7, 123.2, 120.4, 120.3, 119.9, 110.7, 109.6, 57.8. FTIR (ATR)  $\nu$  (cm<sup>-1</sup>): 3049, 2952, 2929, 1625, 1595, 1574, 1495, 1477, 1466, 1450, 1333, 1283, 1228, 1150, 1063, 1016, 917, 872, 801, 746, 722, 652, 640, 615, 558. UV−Vis, [CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{max}$  (nm), ( $\varepsilon$ )]: 268 (9.36 × 10<sup>4</sup>), 292 (7.92 × 10<sup>4</sup>), 342 (2.28 × 10<sup>4</sup>).

1,2-Di-[3,6-di-(9-carbazolyl)-9-carbazolyl]ethane (**7b**). Yield 0.654 g (64%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.16–8.09 (m, 12H, ArH), 7.92 (dd, *J* = 8.6, 1.9 Hz, 4H, ArH), 7.39–7.10 (m, 28H, ArH), 5.11 (s, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 141.5, 139.6, 130.0, 125.9, 125.8, 123.8, 123.1, 120.2, 119.7, 119.5, 109.4, 109.3, 41.6. FTIR (ATR)  $\nu$  (cm<sup>-1</sup>): 3049, 2952, 2925, 2866, 1625, 1595, 1573, 1495, 1477, 1450, 1334, 1313, 1287, 1229, 1157, 1117, 1019, 917, 876, 805, 745, 722, 684, 641, 615, 558. UV–Vis, [CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{max}$  (nm), ( $\varepsilon$ )]: 272 (9.0 × 10<sup>4</sup>), 294 (7.20 × 10<sup>4</sup>), 342 (2.16 × 10<sup>4</sup>).

1,3-*Di*-[3,6-*di*-(9-*carbazolyl*)-9-*carbazolyl*]*propane* **(7c)**. Yield 0.78 g (75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.27 (d, *J* = 1.9 Hz, 4H, ArH), 8.15 (d, *J* = 7.6 Hz, 8H, ArH), 7.69 (d,d J = 8.6 and 1.9 Hz, 4H, ArH), 7.60 (d, *J* = 8.6 Hz, 4H, ArH), 7.38–7.23 (m, 22H, ArH), 4.72 (t, *J* = 7.4 Hz, 4H, CH<sub>2</sub>), 2.92–2.83 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 141.7, 139.9, 130.0, 126.3, 125.9, 123.7, 123.2, 120.3, 120.1, 119.8, 109.8, 109.6, 41.2, 28.3. FTIR (ATR)  $\nu$  (cm<sup>-1</sup>): 3049, 3020, 1626, 1595, 1573, 1495, 1477, 1450, 1334, 1313, 1283, 1229, 805, 747, 722, 641, 616, 559. UV–Vis, [CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{max}$  (mm), ( $\varepsilon$ )]: 264 (1.10 × 10<sup>5</sup>), 294 (9.24 × 10<sup>4</sup>), 342 (2.64 × 10<sup>4</sup>).

1,4-Di-[3,6-di-(9-carbazolyl)-9-carbazolyl]butane **(7d)**. Yield 0.72 g (69%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.27 (s, 4H, ArH), 8.15 (d, *J* = 7.8 Hz, 8H, ArH), 7.70 (d, 1.2 Hz, 8H, ArH), 7.39–7.34 (m, 16H, ArH), 7.30–7.24 (m, 8H, ArH), 4.61 (t, *J* = 7.4 Hz, 4H, CH<sub>2</sub>), 2.37–2.32 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 141.8, 130.1, 129.8, 126.2, 125.9, 123.6, 123.1, 120.3, 120.0, 119.7, 110.0, 109.6. FTIR (ATR) v (cm<sup>-1</sup>): 3047, 2924, 2853, 1625, 1594, 1573, 1494, 1476, 1449, 1334, 1312, 1287, 1230, 808, 745, 720, 642, 622, 563. UV–Vis, [CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{max}$  (nm), ( $\varepsilon$ )]: 270 (8.64 × 10<sup>4</sup>), 294 (6.84 × 10<sup>4</sup>), 343 (1.92 × 10<sup>4</sup>).

1,5-Di-[3,6-di-(9-carbazolyl)-9-carbazolyl]pentane (7e). Yield 0.81 g (76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.26–8.24 (m, 4H, ArH), 8.15 (d, *J* = 7.6 Hz, 8H, ArH), 7.69–7.67 (m, 8H, ArH), 7.38–7.34 (m,

16H, ArH), 7.30–7.24 (m, 8H, ArH), 4.56 (t, J = 7.2 Hz, 4H, CH<sub>2</sub>), 2.28–2.18 (m, 4H, CH<sub>2</sub>), 1.88–1.77 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 141.8$ , 140.1, 129.6, 126.1, 125.8, 123.5, 123.1, 120.3, 120.0, 119.7, 110.0, 109.6, 43.5, 29.2, 25.5. FTIR (ATR) v (cm<sup>-1</sup>): 3047, 2925, 2865, 1625, 1595, 1573, 1494, 1476, 1334, 1313, 1287, 1229, 806, 746, 722, 641, 617, 558. UV–Vis, [CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{max}$  (nm), ( $\varepsilon$ )]: 264 (1.16 × 10<sup>5</sup>), 294 (1.06 × 10<sup>5</sup>), 342 (2.76 × 10<sup>4</sup>).

#### 2.4. Absorption measurements

The absorption spectra of the CT complexes of the compounds 5a, 5b, 7a-7b with acceptors TCNE and TNM in CH<sub>2</sub>Cl<sub>2</sub> were used in determining the equilibrium constants,  $K_{eq}$ , molar absorptivities,  $\varepsilon$ , enthalpies,  $\Delta H$ , and entropies,  $\Delta S$ , of formation. Experiments with TNM were done under dim light to prevent potential photonitration reactions. The  $\varepsilon$  and  $K_{eq}$  values of CT complexations were determined by Benesi-Hildebrand method [17]. For the TCNE-carbazole CT measurements, a solution consisted of 2.0 ml of  $6\times 10^{-2}$  M TCNE and 7.5  $\times 10^{-4}$  M carbazole unit (i.e.  $2.5\times 10^{-4}$  M **5a** and **5b**;  $1.25 \times 10^{-4}$  M **7a**-**7b**) was placed in a 1.0 cm quartz UV cuvette. This was diluted 10 times by the addition of increments of 200  $\mu l$  of the 7.5  $\times$   $10^{-4}$  M carbazole solutions. For the TNM–carbazole CT measurements, a solution containing 0.6 M TNM and 5  $\times$  10<sup>-3</sup> M carbazole unit (i.e. 1.67  $\times$  10<sup>-3</sup> M 5a and 5b;  $8,3 \times 10^{-4}$  M 7a–7b) was diluted with the solution containing  $5 \times 10^{-3}$  M carbazole unit. During the dilutions TCNE-carbazole concentration ratios varied from 80:1 to 40:1 and TNM-carbazole from 120:1 to 60:1. Absorbance changes at the  $\lambda_{CT}$  were recorded after each dilution.

Thermodynamics of the CT associations were investigated using van't Hoff equation by recording absorbance changes near  $\lambda_{CT}$  at temperatures, 7, 10, 13, 16, 19, 22, and 35 °C (±0.1 °C). In a 2.0 ml volumetric flask, a solution containing  $1.0 \times 10^{-2}$  M TCNE and  $1.0 \times 10^{-2}$  M carbazole unit (i.e.  $3.3 \times 10^{-3}$  M **5a** and **5b**;  $1.7 \times 10^{-3}$  M **7a**–**7e**) at 20 °C was prepared. Then, the solution was transferred into an airtight capped quartz UV cell with l = 1 cm and equilibrated at the desired temperature (*ca*. 10 min.) using a peltier temperature controller system. For TNM–carbazole complexations the measurements were performed using  $2.0 \times 10^{-1}$  M TNM and  $2.0 \times 10^{-2}$  M carbazole unit (i.e.  $6.7 \times 10^{-3}$  M **5a** and **5b**;  $3.3 \times 10^{-3}$  M **7a**–**7e**). Measured absorbance values in calculating the thermodynamic constants were corrected by taking into account the expansion/contraction of CH<sub>2</sub>Cl<sub>2</sub> [18] at changing temperatures.

#### 2.5. Computational analysis

Information about the electronic and geometric structures of the donor and acceptor compounds their CT complexes were gathered from their built 3D models which are optimized in gas phase minimum energy state using semi-empirical methods. Structures of the molecules were drawn using ACD/Labs Chem-Sketch 2015 and transferred to Avogadro 1.1.1 molecule editor and visualizer [19]. Prior to quantum chemical calculations the structures were subjected to molecular mechanics modeling using MMFF94 force field [20], steepest descent algorithm and 10<sup>-</sup> convergence criteria. Thereafter geometry optimizations, total energy and molecular orbital calculations were carried out by semi--empirical Austin Model 1 (AM1), Recife Model (RM1), and Parameterization Method 7 (PM7) Hamiltonian and Polack Riberie minimization algorithm using MOPAC2012 [21]. Density functional theory (DFT) single point energy calculations at the Becke's three parameter hybrid method [22,23] with Lee, Yang and Parr correlation (B3LYP) [24] and 6-31G(d) basis set were done on TCNE, TNM and the model compounds 1, 5a, and 5b using the General

Atomic and Molecular Electronic Structure System (GAMESS) [25,26] on Windows 7. The 3–D graphical representations and geometry analyses were done using Visual Molecular Dynamics (VMD) [27] and Mercury 3.7 [28] programs.

# 3. Results and discussion

#### 3.1. Synthesis

3,6-di-(9-carbazolyl)-9-ethylcarbazole (**5a**), 3,6-di-(9carbazolyl)-9-hexylcarbazole (**5b**) and 1,n-di-[3,6-di-(9carbazolyl)-9-carbazolyl]alkanes (n = 1-5) (7a-7e) were prepared as described in Scheme 1 via copper-catalyzed Ullmann coupling reaction of 3,6-diiodo-9-ethylcarbazole (4a), 3,6-diiodo-9-hexylcarbazole (4b) or 1,n-di-(3,6-diiodo-9-carbazolyl)alkanes (6a-6e) with carbazole. The compounds 4b and 6a-6e were synthesized by nucleophilic substitution reaction of 1bromohexane, 1,n-dibromoalkanes (for n = 1, 3-5) or ethylene di(p-toluenesulfonate) (for n = 2) with 3,6-diiodocarbazole in the presence of KOH as the base to generate corresponding 3,6diiodocarbazolide as the nucleophile. Iodination of carbazole and 9-ethylcarbazole at the C3 and C6 positions was done by the method of Tucker using KI and KIO<sub>3</sub> in glacial acetic acid [16]. Our attempts to synthesize first the 3,6-di-(9-carbazolyl)-9H-carbazole dendron and then perform the nucleophilic substitution reactions resulted in little or no vields probably due to the bulkiness of the nucleophile and poor nucleophilicity.

The structures of the donor compounds are elucidated via spectroscopic techniques. As an example, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **7a** are given in Fig. 1. The doublet peak with a long–range coupling at  $\delta = 8.32$  ppm has been assigned to four protons (H–4 in Fig. 1) in the central carbazole moieties, whereas the peak representing the protons of the same kind (H–4') in the peripheric carbazoles appear at  $\delta = 8.16$  ppm as a doublet of triplets. The doublet at  $\delta = 7.92$  ppm (H–1) and doublet of doublets at  $\delta = 7.76$  ppm (H–2) of central rings give strong evidence for the structure, together with relative peak areas. The number of carbon peaks in <sup>13</sup>C NMR, indicating the symmetry in the molecule, also support the structure. One notable difference is that the carbon at C–3 center shifted 11.1 ppm downfield due to the attachment of electronegative nitrogen atom.

The optimized minimum energy molecular structures of the donor and acceptor compounds are given in Fig. 2.

Selected bond lengths, bond angles and torsion angles of the optimized structures of donor molecules computed via semi--empirical methods are listed in Table 1.

The C–C bond lengths and internal bond angles of the carbazole rings of the optimized structures are comparable to the corresponding bond lengths and angles of experimentally determined structures of 9-(4-bromophenyl)-9H-carbazole [29] and 9-ethyl-3,6-bis (1H-imidazol-1-yl)-9H-carbazole [30]. One can see in Table 2 that the applied RM1 method correlates well with the experimental data (r = 0.889 for the bond lengths and r = 0.996 for the bond angles). The C1–C2 and C4–C4a (~1.384 Å) bonds in the benzene rings are found to be the shortest whereas C4a-C4b (~1.440 Å) bond was the longest due to the angular strain in the central pyrrole rings. The internal C4b-C4a-C9a bond angle around 106.5° is another indication of this strain. Also, there is slight increase (~0.68°) in the bond angle C2–C3–C4 of the central carbazole ring compared to that of peripheral ones due to the reduced electron density at the C3 position by the carbazole nitrogen substituent.

Inter–ring dihedral angles can be used to predict morphologies of the molecules (Table 3). The dihedral angles around 49.89–53.57° between the planes of the carbazole rings defined by



Scheme 1. Synthesis of the donor compounds. (i) KI, KIO<sub>3</sub>, CH<sub>3</sub>COOH; (ii) KOH, 1-bromohexane, DMSO; (iii) Cu, K<sub>2</sub>CO<sub>3</sub>, 18-crown-6, 9*H*-carbazole, 1,2-dichlorobenzene; (iv) KOH, 1,n-dibromoalkane (n = 1,3–5) or ethylene di(p-toluenesulfonate), DMSO.

their all thirteen atoms show the tilted geometry of peripheral rings. In **7c** and **7e** where ring systems are separated by three and five–carbon alkylene chains one of the rings is near to perpendicularity ( $80.83^{\circ}$  in **7c** and  $84.86^{\circ}$  in **7e**). This geometry is thought to be adopted to avoid any possible short contact between aromatic hydrogen atoms. In compounds **7a**–**7e** there is a decrease in the dihedral angles of the planes of central carbazole rings as the alkylene chain–length increases. These tilted geometry of the carbazole rings explains the amorphous morphology of the synthesized donor molecules.

# 3.2. Thermal analyses

The thermal properties of the compounds were examined using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under a nitrogen atmosphere. The glass-transition temperatures ( $T_{\rm g}$ ), melting temperatures ( $T_{\rm m}$ ), % weight loss at 250 °C and changes in heat capacity at Tg ( $\Delta C_p$ ) are given in Table 4. Thermogravimetric analyses showed that all of the donor compounds are thermally stabile having  $T_d > 250 \degree C$  with weight losses ranging between 0.59 and 4.66% at 250 °C. All of the compounds are amorphous and did not form any crystals as proven by their DSC curves (Fig. 3). Tg values (103.8-105.0 °C) obtained from the first run heating scan showed that both monomers and dimers bear glass–like morphology.  $\Delta C_p$  values (0.018–0.493 J mol<sup>-1</sup> °C<sup>-1</sup>) of the donor compounds at  $T_{g}$ , calculated from the shift in the baseline at the starting transients, indicate small change in the  $C_p$  values during glass-transition. Results of the thermal analyses suggest these donor compounds' potential application as film-forming materials for opto-electronic applications.

## 3.3. CT absorptions

Carbazole donor molecules form blue colored CT complexes

with TCNE and yellow-brown CT complexes with TNM due to the visible-light irradiation. Mulliken explained this color change with the CT excitation of DA complex associated with an electron transfer from the highest energy molecular orbitals (HOMO) of electron-rich donor molecule to the lowest unoccupied molecular orbital (LUMO) of electron deficient acceptor molecule according to the following hypothetical equation [31].

$$\mathbf{D} + \mathbf{A} \stackrel{K}{\rightleftharpoons} [\mathbf{D}, \mathbf{A}] \stackrel{K_{\mathrm{CT}}}{=} \left[ \mathbf{D}^{+.}, \mathbf{A}^{-.} \right]$$

The absorption spectra of the CT complexes of the donor compounds with  $\pi$ -acceptor TCNE gave one distinct shoulder around 580 nm, which could be related to the molar concentration of the complex at the equilibrium. The tetrahedral geometry of  $\sigma$ -acceptor TNM prevented it to approach closely to the flat carbazole group, hence resulting in weaker DA associations compared to TCNE. Unlike TCNE, TNM does not form bound complexes with condensed aromatic  $\pi$ -systems. The charge-transfer between these type of donor-acceptor molecules occur in a very short time when randomly dispersed molecules come across in solution forming a so called 'contact' complexes. Thus, the CT absorption spectra of the donor compounds with TNM showed a tailing in the visible region without forming a peak maximum. Their  $\lambda_{CT}$  values were determined by relating to those of carbazo-le-TCNE spectra.

The diagram showing CT process between carbazole and TCNE is given in Fig. 4.

Absorption spectra of **7c**, TCNE, TNM, **7c**–TCNE complex and **7c**–TNM complex in CH<sub>2</sub>Cl<sub>2</sub> are shown in Fig. 5. Uncomplexed donor and acceptor compounds do not give absorption at the longer wavelengths than 360 nm while their complexes give CT absorptions at  $\lambda_{CT} > 500$  nm. Strength of a donor–acceptor association mainly depends on the electron affinity (*E*<sub>a</sub>) of the acceptor and ionization potential (*I*<sub>p</sub>) of the donor molecules. Relatively high



Fig. 1. <sup>1</sup>H and <sup>13</sup>C NMR spectra of **7a** showing the aromatic region.

 $E_A$  (2.77–2.9 eV) and planar geometry of TCNE make it a good electron acceptor compared to tetrahedral TNM (1.63–1.8 eV) [32,33]. Ionization potential ( $I_p$ ) of carbazole, measured around 7.6–8.0 [34,35], makes it a fairly good electron donor.

The vertical  $I_p(V)$  values were calculated based on the energy differences between optimized geometry of the radical cation and the respective neutral molecule obtained at the same geometry according to Eq. (1).

$$I_{\mathbf{P}}(\mathbf{V}) = E\left(\mathbf{D}^{\cdot +}\right) - E(\mathbf{D}) \tag{1}$$

where  $I_P(V)$  is the vertical ionization potential, E(D) is the calculated total energy of the donor molecule, and  $E(D^{\bullet+})$  is the calculated total energy of radical cationic form of donor molecule. The calculated  $I_P$  values are compared with the experimentally determined ones obtained from CT absorption spectra according to the following empirical equation derived by Aloisi and Pignataro [36],

$$I_{\rm P} = 5.21 + 1.65 \times 10^{-4} \cdot \bar{v}_{\rm CT(\rm TCNE)}$$
(2)

where  $I_p$  is the ionization potential in eV of the donor compound,  $\bar{v}_{CT(TCNE)}$  is the wavenumber in cm<sup>-1</sup> of the CT band for donor-TCNE complexes in CH<sub>2</sub>Cl<sub>2</sub> solvent. The results are given in Table 5, where carbazole (1) was included for comparison.

One can see in Table 5 that experimentally determined  $I_p$  values are greater than the computed ones using the semi–empirical methods. Among the methods applied PM7 and AM1 generated relatively closer values to the experimentally determined ones compared to and RM1. Since Eq. (2) is derived by relating  $I_p$  of a donor molecule to the CT energy of complex with a particular acceptor (in this case TCNE) [36],  $I_p$  values of **5a**, **5b**, and **7a**–**7e** are the same to a large extend (8.0451–8.0548 eV), due to the similar molecular structures and similar CT complexation behaviors. Loss of H on carbazole nitrogen resulted in slightly higher  $I_p$  values of the donor compounds used in this study than that of carbazole, owing to the decreased electron density of the  $\pi$ –system.

The CT transition energies ( $E_{CT}$ ) of the complexes were calculated according to Eq. (3) derived by Briegleb [37],

$$E_{\rm CT} = (hv_{\rm CT}) = 1243.667 \cdot \lambda_{\rm CT}^{-1} \tag{3}$$

where  $\lambda_{CT}$  is the wavelength of CT band in nanometers. The results listed in Table 5 show that CT transition energies of the carbazole–TCNE complexes are about 0.20 eV less on average than those of carbazole–TNM complexes. This result indicate the smaller HOMO–LUMO gap in the molecules of carbazole–TCNE complexes.



Fig. 2. Energy-minimized (RM1) structures of individual donor and acceptor molecules.

Table 1 Mean bond lengths and angles of calculated structures of **5a**, **5b**, **7a**–**7e**. The experimental data of the related compounds are obtained from the Refs. [29, 30].

	AM1 $\overline{X}(\sigma)$	RM1 $\overline{X}(\sigma)$	PM7 $\overline{X}(\sigma)$	Exp.
Bond lengths (Å)				
C1–C2	1.390(1)	1.384(3)	1.388(3)	1.378
C2-C3	1.417(3)	1.407(3)	1.409(4)	1.403
C3–C4	1.413(2)	1.395(3)	1.399(7)	1.384
C4–C4a	1.384(1)	1.384(3)	1.384(1)	1.391
C4a-C9a	1.445(2)	1.421(3)	1.433(9)	1.412
C9a-C1	1.397(1)	1.393(3)	1.394(2)	1.391
C4a-C4b	1.453(2)	1.441(3)	1.444(5)	1.443
N9-C9a	1.414(4)	1.411(13)	1.410(4)	1.387
C3-N9′	1.407(3)	1.416(2)	1.414(4)	1.430
C1′-C2′	1.395(3)	1.386(1)	1.390(3)	1.386
C2'-C3'	1.398(2)	1.398(1)	1.401(1)	1.403
C3′-C4′	1.394(3)	1.387()	1.392(2)	1.380
C4'-C4a'	1.397(22)	1.385(1)	1.388(4)	1.400
C4a'-C9a'	1.440(19)	1.422(1)	1.432(7)	1.412
C9a'-C1'	1.398(2)	1.392(1)	1.394(2)	1.392
C4a'-C4b'	1.451(2)	1.441(1)	1.445(4)	1.443
N9'-C9a'	1.413(4)	1.409(3)	1.409(2)	1.395
Bond angles (°)				
C1–C2–C3	121.76(14)	120.39(1.12)	120.95(3)	120.91
C2-C3-C4	119.85(27)	121.79(44)	121.57(5)	121.06
C3-C4-C4a	118.94(15)	118.02(1.68)	117.85(4)	118.58
C4-C4a-C9a	120.72(22)	120.29(1.28)	120.50(10)	119.99
C4a-C9a-C1	120.08(15)	121.28(15)	121.14(9)	121.10
C9a-C1-C2	118.65(9)	118.21(1.29)	117.88(5)	118.33
C8a-N9-C9a	107.34(1.33)	107.56(28)	107.62(44)	108.52
N9-C9a-C4a	109.74(63)	109.09(11)	109.24(18)	109.31
C4b-C4a-C9a	106.49(13)	107.06(7)	106.86(3)	106.43
C1′-C2′-C3′	121.66(2)	121.73(4)	121.59(1)	121.70
C2'-C3'-C4'	120.99(10)	121.14(4)	121.08(2)	120.97
C3'-C4'-C4a'	118.96(4)	118.39(1)	118.68(2)	118.56
C4'-C4a'-C9a'	119.90(20)	119.99(7)	119.79(5)	119.54
C4a'-C9a'-C1'	120.48(21)	121.68(11)	121.45(4)	122.00
C9a'-C1'-C2'	118.01(14)	117.06(4)	117.46(2)	117.23
C8a'-N9'-C9a'	107.87(33)	107.31(1.02)	108.18(13)	108.58
N9'-C9a'-C4a'	109.29(10)	107.84(1.02)	108.87(4)	108.75
C4b'-C4a'-C9a'	106.74(7)	107.19(5)	107.00(1)	107.04

The dissociation energies (*W*) of the complexes in their excited states were calculated according to Eq. (4) [38], using CT transition energy ( $E_{CT}$ ) of the corresponding complex, ionization potential of

# Table 2

Pearson correlation coefficients (r) between bond length and angle values obtained by different methods.

Method	AM1	RM1	PM7	Exp. <sup>a</sup>
Bond lengths AM1 RM1	1	0.939 <sup>b</sup> 1	0.974 <sup>b</sup> 0.985 <sup>b</sup>	0.810 <sup>b</sup> 0.889 <sup>b</sup>
PM7 Exp. <b>Bond angles</b>			1	0.869 <sup>b</sup> 1
AM1 RM1 PM7 Exp. <sup>a</sup>	1	0,989 <sup>b</sup> 1	0,993 <sup>b</sup> 0,998 <sup>b</sup> 1	0,992 <sup>b</sup> 0,996 <sup>b</sup> 0,998 <sup>b</sup> 1
r				

<sup>a</sup> Data were obtained from Refs. [29,30].

<sup>b</sup> Correlation is significant at the 0.01 level (2-tailed).

the donor molecule ( $I_P$ ), and electron affinity ( $E_A$ ) of the acceptor molecule.

$$E_{\rm CT} = I_{\rm P} - (E_{\rm A} + W) \tag{4}$$

The results of the calculated dissociation energies are summarized in Table 5. The obtained values of charge transfer excited states dissociation energy of the complexes in CH<sub>2</sub>Cl<sub>2</sub> suggest that the [D<sup>•+</sup>,A<sup>•-</sup>] complexes are stable according to their relatively large dissociation energies. Dissociation to the separated D<sup>•+</sup> and A<sup>•-</sup> and deactivation to their neutral ground states appear to require more energy in the complexes with TNM as their relatively higher *W* values (~4.08 eV) compared to those with TCNE (~3.14).

Experimental evidence suggest that electronic transitions involve frontier orbitals of donor and acceptor molecules. DFT [B3LYP/3–21G(d)] calculated frontier orbitals of individual carbazole (1), **5a**, **5b**, TCNE, TNM and carbazole–TCNE and carbazole–TNM complexes may serve to understand the nature of the CT process among the donor and acceptor molecules. The energies of these orbitals are listed in Table 6. Isosurface plots of HOMO and LUMO of carbazole–TCNE, carbazole–TNM complexes and **5a** and **5b** are shown in Fig. 6.

Molecular orbital plots show that frontier MO's of carbazole and

 Table 3

 Dihedral angles between the planes of the carbazole rings in calculated structures of 5a,5b, 7a-7e with RM1 method.

Rings <sup>a</sup>	5a	5b	7a	7b	7c	7d	7e
A and B A and C A' and B'	51.01 50.90	50.80 52.32	50.47 50.49 50.59	51.43 51.59 51.34	51.00 53.57 49.89	51.81 51.74 52.43	51.50 84.86 51.66
A and A'			50.49 79.40	51.45 48.86	80.83 39.95	30.12	25.69

 $^{\rm a}$  A and A' represent central, B, B', C, and C' peripheral carbazole rings in the molecules.

Table 4

Thermal properties of the compounds 5a, 5b, 7a-7e.

Compound	$T_{\rm g}\left({\rm C}^\circ\right)$	$\Delta C_p$ (J mol <sup>-1</sup> °C <sup>-1</sup> )	$T_{\mathrm{m}}\left(C^{\circ}\right)$	%Weight Loss(at 250 C°)
5a	104.1	0.081	282.6	3.22
5b	104.7	0.036	256.8	0.88
7a	103.9	0.127	256.4	4.66
7b	105.0	0.493	261.7	0.80
7c	103.8	0.054	283.9	1.40
7d	104.6	0.018	289.4	1.25
7e	104.1	0.053	281.2	0.59

TCNE are mainly composed of *p* atomic arobitals, leading to stronger  $\pi_{HOMO} - \pi_{LUMO}$  interactions, whereas TNM involves only  $\sigma$  frontier orbitals. Despite the high positive charge density localization on the central carbon atom TNM's tetrahedral geometry allows it to form weaker  $\sigma - \pi$  contact complexes with aromatic donor molecules. HOMO MO's of **5a** and **5b** shows that each carbazole ring can form complex with one acceptor molecule.

Electron density difference (EDD) between the excited and ground states can be used to interpret the nature of the association between donor and acceptor molecules in CT complexes. For this purpose ground sate and singlet excited state single point energy calculations were performed using the RHF/3–21G(d) method on the same geometry for both states. EDD maps (Fig. 7) of carbazo-le–TCNE and carbazole–TNM complexes it is evident that electron transfer occurs from carbazole (electron donor) to TCNE or TNM (electron acceptor),which explains charge–transfer nature of the complexation.

Inter-molecular distance between donor and acceptor molecules is an indication of the strength of a complexation. Single crystal x-ray diffraction studies show that the distance between carbazole ring and acceptor molecules are about 3.4–3.5 Å [39,40]. Among the optimized geometries of carbazole–TCNE complex PM7 yielded the most successful results in estimating the inter–molecular distance with a centroid–centroid separation of 3.401 Å (AM1 and RM1 methods found it to be 4.390 and 4.087 Å, respectively; Fig. 8). The dihedral angle of 2.50° between the mean planes of donor and acceptor molecules is also in agreement with the observed results indicating  $\pi$ – $\pi$  association.

#### 3.4. Determination of the equilibrium constants of CT complexes

The molar extinction coefficients ( $\varepsilon$ ), and the equilibrium constants ( $K_{eq}$ ) of the charge transfer complexes of the title compounds with the acceptors TCNE and TNM have been determined using Benesi–Hildebrand equation [17] in the form,

$$[D]_0/A = (1/[A]_0) (K_{eq} \varepsilon)^{-1} + (\varepsilon)^{-1} [A]_0 \gg [D]_0$$
(5)

where  $[D]_0$  and  $[A]_0$  are the initial concentrations of the donor and acceptor compounds, respectively, A is the absorbance,  $K_{eq}$  is the equilibrium constant, and  $\varepsilon$  is the molar absorption coefficient of the CT complex at  $\lambda_{CT}$ . Eq. (5) is in the form, y = mx + n, and plotting  $[D]_0/A$  vs.  $1/[A]_0$  will yield ( $K_{eq} \varepsilon$ )<sup>-1</sup> as the slope and ( $\varepsilon$ )<sup>-1</sup> as the intercept. The compound **5a** and **5b** carry three chromophore carbazole groups while **7a**–**7e** include six carbazoles. Earlier studies show that each carbazole group associate with one acceptor molecule [14,41–43]. In this respect, Eq. (5) is rearranged for **5a** and **5b** as:

$$[D]_0 / = (3K_{eq}\varepsilon)^{-1} (1/[A]_0) + (3\varepsilon)^{-1}$$
(6)

and for 7a-7e as:

$$[D]_0/A = (6K_{eq}\varepsilon)^{-1} (1/[A]_0) + (6\varepsilon)^{-1}$$
(7)

Linear Benesi–Hildebrand plots of carbazoles with TCNE and TNM obtained at room temperature are shown in Fig. 9 while  $K_{eq}$  and  $\varepsilon$  values calculated from these plots are summarized in Table 7.

The  $\varepsilon$  values determined from the B–H experiments lie between 498 and 1080 M<sup>-1</sup>cm<sup>-1</sup> ( $\overline{X} = 765 \text{ M}^{-1}\text{cm}^{-1}$ ) for carbazole–TCNE and 74–256 M<sup>-1</sup>cm<sup>-1</sup> ( $\overline{X} = 165 \text{ M}^{-1}\text{cm}^{-1}$ ) for carbazole–TNM CT complexes. Because the aromatic carbazole groups are responsible for the CT complex formations and bound in all the donor



Fig. 3. Part of the DSC curves of the donor compounds. Heating rate: 10 °C min<sup>-1</sup>.



Fig. 4. Schematic frontier orbital energy-level diagram and contour maps for carbazole and TCNE showing CT process.



**Fig. 5.** Absorption spectra of **7c** ( $1 \times 10^{-5}$  M), TCNE ( $1 \times 10^{-4}$  M), TNM ( $1 \times 10^{-4}$  M), **7c**–TCNE complex (formed from  $1 \times 10^{-4}$  M **7c** and  $1 \times 10^{-4}$  M TCNE) and **7c**–TNM complex (formed from  $3,3 \times 10^{-3}$  M **7c** and  $2 \times 10^{-1}$  M TNM) in dichloromethane at 25 °C.

Fable 5
CT transition energy ( $E_{CT}$ ), ionization potential ( $I_P$ ) of the donor molecules, and dissociation energy (W) of CT complexes in CH <sub>2</sub> Cl <sub>2</sub> .

Compound	npound $I_{\rm P}({\rm eV})$ TCNE					TNM					
	Exp. <sup>a</sup>	MNDO	AM1	RM1	PM7	$\lambda_{\rm CT}$ (nm)	$E_{\rm CT} ({\rm eV})$	<i>W</i> (eV)	$\lambda_{\rm CT}$ (nm)	$E_{\rm CT} ({\rm eV})$	<i>W</i> (eV)
1	7.955	7.534	7.876	7.664	7.757	601	2.069	3.116	549	2.265	4.060
5a	8.045	6.993	7.364	6.968	7.230	582	2.137	3.138	532	2.338	4.077
5b	8.045	6.984	7.320	6.959	7.221	582	2.137	3.138	532	2.338	4.077
7a	8.055	7.092	7.318	7.013	7.303	580	2.144	3.141	530	2.347	4.078
7b	8.050	7.025	7.202	6.636	7.228	581	2.141	3.139	531	2.342	4.078
7c	8.050	7.014	7.195	6.642	7.241	581	2.141	3.139	531	2.342	4.078
7d	8.050	7.719	7.266	6.650	7.281	581	2.141	3.139	531	2.342	4.078
7e	8.050	7.632	7.173	6.606	7.211	581	2.141	3.139	531	2.342	4.078

<sup>a</sup> Calculated according to Eq. (2) from the CT absorption spectra.

Table 6	
Frontier orbital energies of the model donors, acceptors and CT complexes of carbazole with both acceptors in ground state.	a,b

	Donor			Acceptor		CT complex		
	1	5a	5b	TCNE	TNM	[1,TCNE]	[1,TNM]	
LUMO+2	1.113(47)	-0.503(141)	-0.574(157)	-1.287(35)	-3.741(52)	-1.029(79)	-3.314(96)	
LUMO+1	0.441(46)	-0.509(140)	-0.580(156)	-1.611(34)	-3.744(51)	-1.363(78)	-3.423(95)	
LUMO	-0.457(45)	-1.050(139)	-1.107(155)	-4.784(33)	-3.913(50)	-4.495(77)	-3.611(94)	
HOMO	-5.350(44)	-4.971(138)	-7.925(154)	-9.086(32)	-9.701(49)	-5.638(76)	-5.439(93)	
HOMO-1	-5.652(43)	-5.165(137)	-5.159(153)	-10.422(31)	-9.703(48)	-5.894(75)	-5.687(92)	
HOMO-2	-6.688(42)	-5.595(136)	-5.633(152)	-10.805(30)	-9.711(47)	-6.963(74)	-6.767(91)	

<sup>a</sup> The calculations are done at B3LYP/6-31G(d) level.

<sup>b</sup> The numbers in parentheses represent the orbital numbers.



Fig. 6. HOMO and LUMO molecular orbital isosurfaces of [1,TCNE], [1,TNM], 5a and 5b.



**Fig. 7.** Electron density difference between excited and ground states of carbazole–TCNE and carbazole–TNM complexes. Cyan and magenta colors indicate negative and positive charge densities, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

compounds in the same way, their molar absorption coefficients should have the same value. Therefore, average of the  $\varepsilon$  values obtained for each CT complexes used in calculating the  $K_{eq}$  values. The low formation constants show weak donor–acceptor association between carbazole–TCNE ( $K_{eq} = 1.83-3.82 \text{ M}^{-1}$ ) and much weaker association between carbazole–TNM ( $K_{eq} = 0.28-0.45 \text{ M}^{-1}$ ). Among the donor molecules **7a** and **7b** have lower formation constants with both donor molecules due to the interference of the tricarbazolyl groups with each other. The compounds **7c**–**7d** behaved more like **5a** and **5b** owing to the greater  $-CH_2$ – chain length.

# 3.5. Determination of enthalpy and entropy changes of CT complexes

Enthalpy and entropy changes of complexes were determined according to the van't Hoff equation, which is based on the determination of  $K_{eq}$  at different temperatures according to Eq. (8).

$$-(\Delta H/R)T^{-1} + (\Delta S/R) = \ln[(A/\varepsilon)/([D]_0 - A/\varepsilon)([A]_0 - A/\varepsilon)]$$
(8)

A plot of  $\ln K_{eq}$  vs. 1/T in Eq. (4) yields  $-\Delta H/R$  as the slope and  $\Delta S/R$  as the intercept. The van't Hoff plots of carbazoles with TCNE and TNM are given in Fig. 10.

The enthalpies and entropies of complex formation calculated from van't Hoff plots and the standard free energy changes ( $\Delta G^{\circ}$ ) calculated from the thermodynamic constants by using Eq. (9).

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{9}$$

are summarized in Table 8. Enthalpies of complexation were determined to be between  $-2.09 \pm 0.08$  and  $-3.10 \pm 0.21$  kcal mol<sup>-1</sup> for carbazole–TCNE complexes and  $-0.91 \pm 0.08$  and  $-3.31 \pm 0.28$  kcal mol<sup>-1</sup> for carbazole–TNM complexes. These results show that the complexations are driven by the exothermic enthalpies.  $\Delta H^{\circ}$  values for the complexation of carbazoles with TCNE ( $\overline{X}$ = -2.71 kcal mol<sup>-1</sup>) were found to be slightly more exothermic than those of TNM ( $\overline{X}$ = -2.13 kcal mol<sup>-1</sup>), meaning that carbazole formed more stable than complexes with TCNE than TNM. Entropies of complexations found to be slightly



Fig. 8. Diagram showing the centroid-centroid separation and dihedral angle between mean planes of carbazole and TCNE in carbazole-TCNE complex optimized by PM7 method.



Fig. 9. Benesi-Hildebrand plots of the complexes of carbazole donors with A) TCNE and B) TNM at 25 °C.

negative, indicating a change to a less disordered state. Despite negative entropies, the negative values of  $\Delta G^{\circ}$  indicate that complex formation of carbazoles with TCNE and TNM are spontaneous. The results are comparable to the results of the earlier studies of related carbazole compounds [14,41–43].

# 4. Conclusion

The electron donor molecules 3,6-di-(9-carbazolyl)-9ethylcarbazole, 3,6-di-(9-carbazolyl)-9-hexylcarbazole and series of a series of 1,n-di-[3,6-di-(9-carbazolyl)-9-carbazolyl]alkanes

Table 7
Values of spectrophotometrically determined absorption maxima ( $\lambda_{CT}$ ), molar absorptivity ( $\varepsilon_{CT}$ ) and equilibrium constant ( $K_{eq}$ ) for each of the CT complexations in CH <sub>2</sub> Cl <sub>2</sub> at
25 °C.

Acceptor	Donor	Solvent	T (K)	[A] <sub>0 (M)</sub>	[D] <sub>0 (M)</sub>	$\lambda^a$ (nm)	$\lambda_{CT}^{b}(nm)$	$\varepsilon_{\rm CT} ({ m M}^{-1}{ m cm}^{-1})$	$K \epsilon_{\rm CT} ({ m M}^{-2}~{ m cm}^{-1})$	$K_{\rm CT}$ (l mol <sup>-1</sup> )
TCNE	5a	CH <sub>2</sub> Cl <sub>2</sub>	295	0.06	$2.50  imes 10^{-4}$	342	582	765	2600 ± 36	3.40
	5b				$2.50  imes 10^{-4}$	343	582		2920 ± 93	3.82
	7a				$1.25  imes 10^{-4}$	342	580		1480 ± 32	1.83
	7b				$1.25  imes 10^{-4}$	342	581		1500 ± 39	1.96
	7c				$1.25  imes 10^{-4}$	342	581		2180 ± 57	2.85
	7d				$1.25  imes 10^{-4}$	343	581		$1780 \pm 27$	2.33
	7e				$1.25  imes 10^{-4}$	342	581		2355 ± 50	3.08
TNM	5a	$CH_2Cl_2$	295	0.6	$1.67 \times 10^{-3}$	342	532	165	$73.4 \pm 1.4$	0.45
	5b				$1.67 \times 10^{-3}$	343	532		57.4 ± 1.7	0.35
	7a				$8.33  imes 10^{-4}$	342	530		$48.4 \pm 1.0$	0.29
	7b				$8.33  imes 10^{-4}$	342	531		$45.5 \pm 0.4$	0.28
	7c				$8.33  imes 10^{-4}$	342	531		59.8 ± 2.2	0.36
	7d				$8.33  imes 10^{-4}$	343	531		$70.7 \pm 0.5$	0.43
	7e				$8.33\times10^{-4}$	342	531		$60.0\pm3.0$	0.36

<sup>a</sup> Lowest enrgy absorption maximum of the donor molecule (nm).
 <sup>b</sup> Lowest energy CT maximum (nm)



Fig. 10. Van't Hoff plots of the complexes of carbazole donors with A) TCNE and B) TNM at 25  $^\circ$ C.

Acceptor	Donor	Solvent	$\Delta H$ (kcal mol <sup>-1</sup> )	$\Delta S$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^{\circ}$ (kcal mol <sup>-1</sup> ) (298 K)
TCNE	5a	CH <sub>2</sub> Cl <sub>2</sub>	$-2.09 \pm 0.08$	$-2.14 \pm 0.29$	-1.45
	5b		$-2.84 \pm 0.28$	$-6.89 \pm 0.95$	-0.79
	7a		$-2.99 \pm 0.11$	$-6.72 \pm 0.39$	-0.99
	7b		$-2.98 \pm 0.10$	$-6.08 \pm 0.35$	-1.17
	7c		$-2.73 \pm 0.14$	$-4.99 \pm 0.48$	-1.24
	7d		$-2.22 \pm 0.21$	$-3.69 \pm 0.74$	-1.12
	7e		$-3.10 \pm 0.21$	$-6.36 \pm 0.73$	-1.20
TNM	5a	$CH_2Cl_2$	$-2.00 \pm 0.07$	$-4.86 \pm 0.24$	-0.55
	5b		$-1.80 \pm 0.07$	$-4.07 \pm 0.26$	-0.59
	7a		$-0.91 \pm 0.08$	$-0.31 \pm 0.29$	-0.82
	7b		$-2.13 \pm 0.13$	$-4.58 \pm 0.46$	-0.77
	7c		$-3.31 \pm 0.28$	$-6.89 \pm 0.97$	-1.26
	7d		$-2.97 \pm 0.17$	$-6.10 \pm 0.58$	-1.15
	7e		$-1.77 \pm 0.13$	$-2.29 \pm 0.46$	_1.09

**Table 8** Values of spectrophotometrically determined enthalpy changes ( $\Delta H$ ), entropy changes ( $\Delta S$ ), and standard free energy changes ( $\Delta G^{\circ}$ ) of the CT complexations

were synthesized via copper-catalyzed Ullmann coupling reaction of corresponding iodocarbazoles. DSC analyses showed that all seven donor compounds exhibited amorphous structure with  $T_{\sigma}$ values between 103.8 and 105.0 °C. Structures of the donor compounds calculated by semi-empirical methods supported their amorphous morphology. They formed stable intermolecular CT complexes with the electron acceptors TCNE and TNM in dichloromethane. The frontier molecular orbitals of model compounds calculated by B3LYP/6-31G(d) method electron density difference maps of carbazole-TCNE and carbazole-TNM calculated using RHF/6-31G(d) method provided valuable data to interpret experimentally observed CT complexation behavior of these compounds. The low equilibrium constants, K<sub>eq</sub>, of the complexations determined by the linear Benesi-Hildebrand method show weak CT association between donor and acceptor molecules. Among the dimeric donor molecules **7a** and **7b** have the smaller  $K_{eq}$  values in each case due to the steric reasons. The enthalpies and entropies of complex formations calculated utilizing van't Hoff plots show that these complexes govern some thermodynamic stability, which is driven by exothermic reaction heats despite the negative  $\Delta G$  values. Considering these properties of the investigated compounds they can have practical use in optoelectronic applications.

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