Novel thiophene-containing *push-pull* chromophores that include carbazole and triphenylamine moieties: study of optical and electrochemical properties

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Novel carbazole- and triphenylamine-containing alkylidene malononitriles that include thiophene and bithienyl fragments as π -spacers were synthesized. Quantum-chemical calculations of the frontier molecular orbital energies were performed using the B3LYP/6-31G(d) method with regard to solvent. Electronic absorption spectra and fluorescence spectra were recorded for all the obtained compounds; their electrochemical properties were also studied. The experimental energy values of HOMO and LUMO levels were derived from resulting data. Thin films were obtained by the spin coating technique, and their surface morphology was studied using a NTEGRA Prima scanning tunneling microscope.

Keywords: alkylidene malononitrile, carbazole, thiophene, triphenylamine, B3LYP/6-31G(d) method, chromophore, electrochemical properties, optical properties.

Organic photovoltaic cells are attracting increased attention as an alternative to traditional silicon solar cells,^{1,2} due to the possibility of using low-cost production techniques to create a large area of multilayer structures on flexible substrates.³⁻⁵ There are two basic configurations of organic photovoltaic cells: the planar-type battery in which the photoactive components are applied in separate layers, and the bulk-heterojunction battery in which there is only one photoactive layer in the form of a mixture of the donor and acceptor.⁶ It is known that the highest efficiency for solar cells with bulk-heterojunction has been achieved in the narrow band gap polymers.⁷⁻¹⁰ Despite the significant progress reached in the field of optimization of the bulkheterojunction solar cell characteristics, the use of polymeric materials in this area is limited due to the difficulties of purification, complexity of controlling the ordering of the structure, as well as a wide molecular weight

distribution.^{11,12} These factors reduce the overall efficiency and stability of the devices.¹³

Small-molecule solar cells are now becoming an alternative to polymer-based solar cells. On the one hand, they exhibit properties inherent to polymers such as flexibility, processability, the ability to form products from solutions. On the other hand, these small molecules have a constant molecular weight and their structure is strictly defined by the fact that these compounds can be purified to a high degree.¹⁴⁻¹⁸ To achieve high efficiency for bulkheterojunction photovoltaic cells, it is crucial to develop new types of π -conjugated small molecules with a narrow band gap, which is important for the efficient absorption of sunlight, and with a high charge carrier mobility to transport photogenerated charges to the electrodes.¹² At present, much attention is paid to the synthesis and study of organic molecules of D- π -A structure, which is due to the possibility Scheme 1



to tune the optical and electronic properties of these systems by varying the electron-donating and electronaccepting moieties contained within their structure and by introducing π -linkers of different nature, which, in turn, allows to expand the range of absorption due to intramolecular charge transfer from the donor to the acceptor moiety.¹⁸⁻²⁰ It has been repeatedly shown that the presence of such fragments as carbazole, triphenylamine, and thiophene within the semiconductor structure helps to reduce the width of the band gap, resulting in the improvement of transporting and photovoltaic properties due to efficient intramolecular charge transfer.^{15,21,22}

This work presents the synthesis of novel D- π -A structures containing electron-donating carbazole and triphenylamine fragments, as well as the results of the study of their properties. Dicyanovinylene moiety, capable of increasing the electron affinity of the molecule of the compound as a whole and reducing the band gap of the conjugated system, was used as an acceptor (A). Thiophene and bithienvl were selected as π -spacers for these molecules in order to reduce the width of the band gap, contributing to a stronger light absorption and expansion of the absorption spectrum.²³ This was confirmed by the experimental data obtained by Japanese researchers, according to which the introduction of an additional thiophene ring in the structure of the molecule leads to a bathochromic shift of 20 nm of the maximum absorption band. However, on increasing the conjugated chain to four

Scheme 2

and more thiophene rings, such a shift disappears.²⁴ There are various methods for extension of the conjugated chain by introducing various aryl and hetaryl fragments into the structure of compounds mainly *via* metal-catalyzed reactions,²⁵⁻²⁸ competing with photocatalyzed CH hetero-arylation reactions.^{29,30} We selected two synthetic approaches for the introduction of thiophene and bithienyl fragments into the conjugated chain. In the first case, the Suzuki coupling of (9*H*-carbazol-9-yl)phenylboronic acid (**2**), synthesized by the previously described method,²² with brominated thiophenecarbaldehydes **3**, **4** in the presence of Pd(PPh₃)₄ and Na₂CO₃ as the base (Scheme 1) was used. As a result, aldehydes **5**, **6** were obtained.

The second method, based on the Vilsmeier–Haack– Arnold acylation, presents a two-stage process, as a result of which an additional acetyl thiophene fragment is formed (Scheme 2). Initially, chloropropenals **8**, **10** were synthesized by interaction of phosphorus oxychloride, DMF, and the corresponding methyl ketones **7** and **9**, whose further reaction with sodium sulfide in DMF and subsequent treatment of the intermediate products with chloroacetone resulted in the formation of 3-acetonyl-3-arylthiopropenals. The cyclization of the latter by the action of a base (K₂CO₃) afforded 5-acetyl-5-arylthiophenes **9**, **11**. The starting 1-(4-diphenylaminophenyl)ethanone (**7**), chloropropenal **8**, and {5-[4-(*N*,*N*-diphenylamino)phenyl]thiophen-2-yl}ethanone (**9**) were obtained previously,³¹ the methods of their synthesis was used in the present work.



Scheme 3



Subsequent reaction of aldehydes **5**, **6**, **9** or ketones **11** with malononitrile in benzene in the presence of catalytic amounts of ammonium acetate and acetic acid resulted in the corresponding 2-(arylmethylidene)malononitriles **12**, **13** and 2-(1-arylethylidene)malononitriles **14**, **15** (Scheme 3).

Conjugated systems **12–15** were synthesized with an aim to determine their potential as materials for bulk-heterojunction organic solar cells. To do this, the quantumchemical calculations of molecular orbital energies using the B3LYP/6-31G(d) method taking into account the effect of the solvent (chloroform, within the DPCM model) was initially performed using the Firefly software^{32,33} on a GPU Tesla supercomputer. The geometry of the molecules was preliminary optimized by the same method.

Calculations has shown that compounds 14, 15 with triphenylamine moiety are characterized by large values for the energies of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals, compared with the corresponding values found for carbazole compounds 12 and 13. Introducing of a second thiophene ring to the structure of compounds 12, 14 increases electron-donating properties of the systems that results in increasing of the HOMO level, whereas the LUMO energy level changes insignificantly. These parameters are important for the calculation of the efficiency of the solar battery.³⁴ It is known that the energy gap between the LUMO level of an electron-donating component of the solar cell (compound with D- π -A structure) and the LUMO level of soluble derivatives of fullerene (PCBM [60] or PCBM [70]), often used as an electron-accepting component, should be 0.3 eV. With a larger value, significant losses in the open-circuit voltage (V_{oc}) and light conversion efficiency (η) occur. To achieve the maximum open circuit voltage, it is also important to adjust the HOMO level energy of the donor material to a value of about -5.5 eV.^{35,36}

Figure 1 shows the geometry of the HOMO and LUMO. The electron density of the HOMO orbitals of all compounds is located on the donor groups containing carbazole, triphenylamine, and thiophene fragments. It has been found that the largest electron density is concentrated on the nitrogen atom. For compounds **12**, **14**, the electron density in the LUMO orbitals is located mainly on the acceptor moiety, whereas for compounds **13**, **15**, it is located on the acceptor moiety and in part on the thiophene linker.

To compare the data obtained by calculations with experimental data, we investigated the optical and electrochemical properties of the synthesized compounds **12–15**. Absorption spectra and fluorescence spectra were recorded for solutions of the compounds in chloroform. The HOMO–LUMO gap (E_g^{opt}) was calculated on the base of the absorption spectrum edge value (λ_{onset}^{abs}) by the formula:

$$E_{g}^{opt} = 1241/\lambda_{onset},$$

where λ_{onset} – wavelength of the absorption spectrum edge. 37

Stokes shifts were calculated as the difference of the wavelengths of the absorption and fluorescence maxima (Table 1). This value indicates the amount of energy that is consumed by a molecule in nonradiative processes, which is important to determine the material of an organic electronic device.

Figure 2 shows the absorption and emission spectra of compounds 12–15. There are four peaks (λ_{max}^{abs}) in the region of 280–550 nm in the UV absorption spectra of compounds 12 and 13. Absorption maxima at 294, 327, 341 nm (compound 12) and at 295, 329, 342 nm (compound 13) can be attributed to π - π * electronic transitions. The long-wavelength absorption maxima at 433 nm (compound 12) and 450 nm (compound 13) arise as a



Figure 1. The energies of HOMO and LUMO levels of compounds **12–15** and their visualization after optimization in the FireFly program using the B3LYP/6-31G(d) method.

Table 1. Spectral characteristics of compounds 12-15

Com- pound	λ_{\max}^{abs*} , nm	$\lambda_{onset}^{abs},$ nm	$\lambda_{max}^{em**},$ nm	Stokes shift , nm	$E_{\rm g}^{\rm opt}$, eV
12	294, 327, 341, 433	510	545	112	2.43
13	295, 329, 342, 450	549	599	149	2.25
14	307, 465	569	611	146	2.17
15	303, 357, 477	604	656	179	2.05

* λ_{max}^{abs} – values of absorption maximum wavelength.

** λ_{max}^{em} – values of emission maximum wavelength.

consequence of the existence of intramolecular charge transfer (ICT) from a donor to the dicyanovinylene acceptor moiety.¹⁵ Furthermore, the introduction of additional thiophene fragments in the structure of compound **13** led to a bathochromic shift of 17 nm of the long-wavelength absorption maximum. The absorption spectra of compounds **14** and **15** exhibit two (compound **14**) and three (compound **15**) absorption maxima in 285–670 nm range. Shortwave absorption peaks in the spectra of compounds **14** (307 nm) and **15** (303, 357 nm) are related to the π - π * transition; long-wavelength absorption maxima at 465 nm (compound **14**) and 477 nm (compound **15**) result from intramolecular charge transfer.³⁸

Anomalously high values of the Stokes shift were observed for all of the obtained compounds. The highest values were found for compounds 14 and 15, due to the fact that structures containing triphenylamine moiety tend to form a twisted conformation when excited, whereby part of the energy is spent on geometric relaxation.³⁹

The electrochemical properties of the synthesized compounds **12–15** were investigated by cyclic voltammetry (CV) using a MeCN–CH₂Cl₂, 9:1 (v/v), mixture (Figs. 4, 5 and Table 2) as the medium. Based on the experimental results, the energy of the frontier orbitals (HOMO, LUMO) was calculated. To evaluate the energy levels of the HOMO and LUMO, the potentials for onset of oxidation (E_{ox}^{onset}) were determined.

Formulas (1) and (2) were used for the calculations:

$$E_{\rm HOMO} = -(E_{\rm ox}^{\rm onset}_{\rm vs \, Ag/AgCl} - E_{\rm Fc \, vs \, AgCl} + 4.8) \, \rm eV$$
(1),

where $E_{\rm Fc \, vs \, AgCl} = +0.41;^{40}$

$$E_{\rm LUMO} = E_{\rm HOMO} + E_{\rm g}^{\rm op} \, \rm eV \tag{2}.$$

Due to presence in the structure of compounds 12 and 13 of an unsubstituted carbazole moiety, these compounds are able to undergo electrochemical oligomerization on the surface of the working electrode.²² Redox processes in compounds 12 and 13 occur in the range of 0.6 to 1.6 V and from 0.8 to 1.7 V, respectively. The presence of two reversible oxidation peaks indicates the initial formation of a carbazole radical cation, which is converted to the



Figure 2. *a*) Absorption spectra of compounds **12** (solid line) and **13** (dotted line); *b*) absorption spectra of compounds **14** (solid line) and **15** (dotted line) (solvent $CHCl_3$, *c* 10^{-5} mol/l).



Figure 3. *a*) Emission spectra of compounds **12** (solid line) and **13** (dotted line); *b*) emission spectra of compounds **14** (solid line) and **15** (dotted line) (solvent $CHCl_3$, *c* 10^{-5} mol/l).



Figure 4. Cyclic voltammetry curves of compounds *a*) **12** and *b*) **13** (carbon pyroceramics working electrode, $\text{Et}_4\text{N}^+\text{ClO}_4^-$, V_{scan} 50 mV·s⁻¹, MeCN–CH₂Cl₂, 9:1, 10 cycles).



Figure 5. Cyclic voltammetry curves of compounds *a*) 14 and *b*) 15 (carbon pyroceramics working electrode, $\text{Et}_4\text{N}^+\text{ClO}_4^-$, V_{scan} 50 mV·s⁻¹, MeCN–CH₂Cl₂, 9:1, 10 cycles).

corresponding dication. The next irreversible oxidation peak indicates the formation of oligomers on the electrode surface. Based on these data, it was revealed that compounds **12** and **13** have sufficiently deep HOMO levels, values of which are significantly below the air oxidation threshold (about -5.2 eV), which in turn provides a good air stability for the molecules and increases the open circuit voltage (V_{oc}) of the solar cell.^{18,42}

It is known that structures containing triphenylamine (TPA) fragment are electrochemically active, and that triphenylamine dimerizes with the loss of two protons to form N,N,N', N'-tetraphenyl-4,4'-diaminobiphenyl (tetraphenyl-benzidine, TPB) as a result of electrochemical oxidation.^{43,44} Three peaks on the anode curve and two peaks on the cathode curve usually present on a CV curve of triphenylamine. The first oxidation peak corresponds to

the formation of the radical cation (TPA⁺⁻), which rapidly dimerizes to form tetraphenylbenzidine. The next peak corresponds to the formation of radical cation (TPB⁺⁻). further oxidation of which leads to a dication (TPB^{2+}) . Its formation is evidenced by the appearance of a third peak on the CV curve, with such separation of the peaks characteristic only for the first wave of oxidationreduction. The first oxidation peak always remains reversible. In our case, three reversible oxidation peaks are observed on the CV curves for compounds 14, 15 (Table 2), with the latter two becoming gradually smoothed under multiple potential scans. The first reversible oxidation peak $(E_{\rm ox}^{-1})$ describes the formation of the corresponding radical cation of triphenylamine, which is stable presumably due to the presence of a conjugated chain in the structure of molecules. This cation radical further dimerizes to form a

Table 2. The values of oxidation and reduction potentials, ionization potentials and electron affinities of compounds 12–15(MeCN-CH₂Cl₂, 9:1, bulk electrolyte $Et_4N^+ClO_4^-$)

Com- pound	$E_{\rm ox}^{1*}$, B	$E_{\rm ox}^{2*}$, B	$E_{\rm ox}^{3*}$, B	$E_{\rm red}^{1}$ **, B	$E_{\rm red}^{2}$ **, B	$E_{\rm red}^{3**}$, B	$E_{\rm ox}^{\rm onset}$, B	HOMO, eV	LUMO, eV
12	0.68	0.93	1.61	0.48	0.75	-	1.32	-5.71	-3.28
13	0.87	1.33	1.70	0.65	1.21	-	1.17	-5.56	-3.31
14	1.03	1.23	1.65	0.97	1.19	1.61	0.91	-5.30	-3.13
15	0.99	1.31	1.71	0.87	1.25	1.67	0.81	-5.20	-3.15

* E_{ox}^{1-3} – value of oxidation wave potential.

** $E_{\rm red}^{1-3}$ – value of reduction wave potential.



Fig. 6. 2D-STM image of surface films of compounds 12–15, scan size $1 \times 1 \mu m$.

substituted tetraphenylbenzidine, and the following two peaks are related to oxidation of the TPB fragment (cation radical, dication).

Thin films of compounds 12–15 were obtained on an ITO substrate by spin coating technique from chlorobenzene solution (5 mg/ml). The structure of the films was studied using scanning tunneling microscopy (NTEGRA Prima – Modular (AFM, STM) system). All measurements were carried out under standard conditions; a voltage of 0.1 V was applied on the scanning probe (palladium wire) and a current of ~0.5 nA was maintained. Examples of the obtained images demonstrates a sufficiently smooth surface for the obtained films, without large crystalline domains. The average particle size was 30 nm (Fig. 6).

To conclude, we have synthesized novel substituted alkylidene malononitrile structures which can be described as $Cz-C_6H_4-Th_n-CH=C(CN)_2$ and $Ph_2N-C_6H_4-Th_n-C(Me)=C(CN)_2$ (Cz = 9H-carbazol-9-yl, Th = thiophen-2-yl, n = 1, 2) and which can be considered as potential materials for bulk-heterojunction solar cells. The results of quantum-chemical calculations of the energies of frontier molecular orbitals were corroborated by experimental data, according to which the synthesized compounds have a narrow band gap of 2.43-2.05 eV. It was found that the resulting compounds have good film-forming properties, yielding thin films of good quality with a smooth surface.

Experimental

IR spectra were registered on a Specord 75 IR spectrometer in $CHCl_3$ (compounds 13–15) or in petroleum jelly (remaining compounds). UV spectra were recorded on

a Shimadzu UV-2600 spectrophotometer, 10-mm cuvettes, solvent – abs. $CHCl_3$, concentration 10^{-5} M. Fluorescence spectra were recorded on a Shimadzu RF-5301 spectrofluorometer. Excitation wavelength 220 nm, cuvette dimensions 10×10 mm, solvent - abs. CHCl₃, concentration 10⁻⁵ M. ¹H NMR spectra were acquired on a Varian Mercury plus300 spectrometer (300 MHz) in CDCl₃, internal standard hexamethyldisilazane (0.037 ppm). Signals of the carbazole protons are denoted as Cz, signals of the thiophene protons as Th. Mass spectra were recorded on a Agilent GC 6890N MSD 5975B LC-MS system, EI ionization (70 eV). Elemental analysis was performed on a CHNS-932 apparatus (LECO Corporation), chlorine content was determined using the Schöniger method.45 Monitoring of the reaction progress and assessment of the purity of synthesized compounds were done by TLC (Sorbfil). Separation of mixtures and purification of target compounds were performed by column chromatography on silica gel (Lancaster, Silica gel 60, 0.060-0.200 mm), the diameter of the column and the height of the silica gel layer were determined by the amount of the substance to be purified. The method of cyclic voltammetry was used to perform the electrochemical studies of the synthesized compounds. The measurements were performed on a Gamry Interface1000 potentiostat in a three-electrode cell with carbon pyroceramics working electrode, a platinum auxiliary electrode, and silver chloride reference electrode. Solutions of the samples in 10 ml of a mixture of abs. MeCN and CH₂Cl₂, 9:1, were used in the studies, supporting electrolyte 0.1 M Et₄N⁺ClO₄⁻. Studies of the structure of the films was done on the NTEGRA Prima scanning probe microscope, in scanning tunneling microscopy mode. Deposition of the film was done in an argon-filled sealed glove box Nitrogen Glove Box PlasLabs, spin coater SPIN 12000.

Compounds 1, 2, 7–9 were synthesized according to published methods. 18,27

Synthesis of compounds 5, 6 (General method). A mixture of bromo-substituted aldehyde 3, 4 (0.02 mol), 4-(9*H*-carbazol-9-yl)phenylboronic acid (2) (5.74 g, 0.02 mol), Pd(PPh₃)₄ catalyst (3% by weight of bromo-substituted aldehyde), PhH (20 ml), and 2 M aqueous Na₂CO₃ (10 ml) was heated under reflux under argon for 24 h. Upon completion of the reaction (monitoring by TLC), the mixture was cooled to room temperature and the organic phase was separated. The aqueous phase was extracted with CH₂Cl₂, the organic phases were combined and concentrated. The residue was purified by column chromatography (eluent CH₂Cl₂).

5-[4-(9*H***-Carbazol-9-yl)phenyl]thiophene-2-carbaldehyde** (5). Yield 0.57 g (81%), yellow-green crystals, mp 194– 196°C. IR spectrum, v, cm⁻¹: 1696 (C=O). ¹H NMR spectrum, δ , ppm (*J*, Hz): 7.30 (2H, t, *J* = 9.0, H-3,6 Cz); 7.39 (2H, d, *J* = 9.0, H-1,8 Cz); 7.44 (2H, t, *J* = 9.0, H-2,7 Cz); 7.46 (1H, d, *J* = 4.6, H-3 Th); 7.64 (2H, d, *J* = 9.6, H-2,6 C₆H₄); 7.77 (1H, d, *J* = 4.3, H-4 Th); 7.88 (2H, d, *J* = 9.3, H-3,5 C₆H₄); 8.13 (2H, d, *J* = 8.6, H-4,5); 9.92 (1H, s, CHO). Mass spectrum, *m*/*z* (*I*_{rel}, %): 354 [M+H]⁺ (26), 353 [M]⁺ (100), 280 (11), 176 (12), 140 (9). Found, %: C 78.08; H 4.31; N 3.99; S 9.13. C₂₃H₁₅NOS. Calculated, %: C 78.16; H 4.28; N 3.96; S 9.07.

2-{5'-[4-(9*H***-Carbazol-9-yl)phenyl]-2,2'-bithiophen-5-yl}-2-carbaldehyde (6)**. Yield 0.65 g (75%), yelloworange powder, mp 141–144°C. IR spectrum, v, cm⁻¹: 1662 (C=O). ¹H NMR spectrum, δ , ppm (*J*, Hz): 7.17 (1H, d, *J* = 4.6, H-4' Th); 7.30 (2H, t, *J* = 8.6, H-3,6 Cz); 7.33 (2H, d, *J* = 9.0, H-1,8 Cz); 7.35 (1H, d, *J* = 4.0, H-3' Th); 7.38 (1H, d, *J* = 4.0, H-4 Th); 7.44 (2H, t, *J* = 8.6, H-2,7 Cz); 7.62 (2H, d, *J* = 9.3, H-2,6 C₆H₄); 7.70 (1H, d, *J* = 4.3, H-3 Th); 7.83 (2H, d, *J* = 10.0, H-3,5 C₆H₄); 8.14 (2H, d, *J* = 8.3, H-4,5 Cz); 9.88 (1H, s, CHO). Mass spectrum, *m/z* (*I*_{rel}, %): 437 [M+2H]⁺ (13), 436 [M+H]⁺ (31), 435 [M]⁺ (100), 217 (10), 181 (11). Found, %: C 74. 49; H 3.90; N 3.27; S 14.65. C₂₇H₁₇NOS₂. Calculated, %: C 74.45; H 3.93; N 3.22; S 14.72.

3-Chloro-3-{5-[4-(diphenylamino)phenyl]thiophen-2-yl}prop-2-enal (10). POCl₃ (1.15 ml, 12 mmol) was slowly added to DMF (1.30 ml, 17 mmol) at 0°C, the mixture was stirred at 0°C for 10 min. Then a solution of ketone 9 (3.69 g, 10 mmol) in DMF (15 ml) was added dropwise, and the reaction mixture was stirred at 60°C for 3 h. After cooling the mixture, 10% aqueous NaOAc was added until pH 4. 3-Aryl-3-chloroprop-2-enal 10 that separated was filtered off, washed with water. An analytical sample was purified by chromatography (eluent CH₂Cl₂), the rest used in the synthesis without additional purification. Yield 1.33 g (80%), slowly crystallizing dark-red mass, mp 96–97°C. IR spectrum, v, cm⁻¹: 1661 (CHO). ¹H NMR spectrum, δ, ppm (*J*, Hz): 6.54 (1H, d, *J* = 6.6, C(Cl)=CH–CHO); 7.04 (2H, d, J = 8.7, H-3,5 C₆H₄); 7.09 (2H, t, J = 7.5, H-4,4' Ph); 7.11 (4H, d, J = 8.7, H-2,2',6,6' Ph); 7.20 (1H, d, J = 4.2, H-4 Th); 7.28 (4H, t, J = 7.2, H-3,3',5,5' Ph); 7.44 (2H, d,

 $J = 9.0, H-2,6 C_6H_4$); 7.61 (1H, d, J = 3.9, H-3 Th); 10.11 (1H, d, J = 6.9, CHO). Mass spectrum, m/z (I_{rel} , %): 417 [M (${}^{37}Cl$)]⁺ (42), 416 [M(${}^{37}Cl$)+H]⁺ (30), 415 [M(${}^{35}Cl$)]⁺ (100), 382 (10), 381 (31), 380 (94), 352 (18), 351 (27), 273 (13), 190 (48), 176 (12), 168 (13), 167 (22), 139 (11), 77 (13).

1-{5'-[4-(Diphenylamino)phenyl]-2,2'-bithiophen-5-yl}ethanone (11). 3-Aryl-3-chloroprop-2-enal (10) (3.54 g, 8.5 mmol) was added to a solution of $Na_2S \cdot 9H_2O$ (2.00 g, 8.5 mmol) in DMF (15 ml). The reaction mixture was stirred at 60°C for 3 h, then chloroacetone (0.7 ml, 8.5 mmol) was added dropwise and stirring at 60°C continued for 2 h. A solution of K₂CO₃ (1.20 g, 8.5 mmol) in H₂O (1 ml) was added. The mixture was stirred at 60°C for 10 min, then cooled to room temperature, and poured in water. The formed precipitate was filtered off, washed with water, and purified by chromatography (eluent CH₂Cl₂). Yield 2.9 g (76%), dark-yellow crystals, mp 149-150°C. IR spectrum, v, cm⁻¹: 1647 (C=O). ¹H NMR spectrum, δ , ppm (J, Hz): 2.54 (3H, s, COCH₃); 7.05 (1H, d, J = 3.6, H-4' Th); 7.06 (2H, d, J = 8.7, H-3,5 C₆H₄); 7.10–7.14 (6H, m, H-2,2',4,4',6,6' Ph); 7.15 (1H, d, J = 4.2, H-3' Th); 7.27 (4H, t, *J* = 6.6, H-3,3',5,5' Ph); 7.29 (1H, d, *J* = 3.6, H-4 Th); 7.44 (2H, d, J = 8.7, H-2,6 C₆H₄); 7.57 (1H, d, J = 4.2, H-3 Th). Found, %: C 74.54; H4.63; N 3.16; S 14.13. C₂₈H₂₁NOS₂. Calculated, %: C74.47; H 4.69; N 3.10; S 14.20.

Synthesis of compounds 12–15 (General method). A mixture of aldehyde 5, 6 or ketone 9, 11 (5 mmol), $CH_2(CN)_2$ (0.33 g, 5 mmol), glacial AcOH (0.12 ml), and NH_4OAc (40 mg) in PhH (5 ml) was heated under reflux for 10 h in the Dean–Stark apparatus. Additional $CH_2(CN)_2$ (0.33 g, 5 mmol), AcOH (0.12 ml), and NH_4OAc (40 mg) were added, and heating under reflux continued for 10 h. The mixture was then cooled to room temperature, diluted with EtOAc (30 ml), washed with H_2O (25 ml), followed by saturated aqueous NaCl (4 ml), and dried over anhydrous Na₂SO₄. The extract was filtered and concentrated under reduced pressure. The final product was separated by column chromatography, eluent CH_2CI_2 .

2-({5-[4-(9*H***-Carbazol-9-yl)phenyl]thiophen-2-yl}methylidene)malononitrile (12). Yield 1.28 g (64%), orange powder, mp 258–260°C. IR spectrum, v, cm⁻¹: 2217 (C=N). UV spectrum, \lambda_{max}, nm (log \varepsilon): 294 (4.18), 327 (3.95), 341 (4.03), 433 (4.41). Fluorescence spectrum, \lambda_{max}, nm: 545. ¹H NMR spectrum, \delta, ppm (***J***, Hz): 7.32 (2H, t,** *J* **= 9.0, H-3,6 Cz); 7.41 (2H, d,** *J* **= 9.0, H-1,8 Cz); 7.46 (2H, t,** *J* **= 9.6, H-2,7 Cz); 7.53 (1H, d,** *J* **= 4.6, H-4 Th); 7.77 (1H, d,** *J* **= 4.6, H-3 Th); 7.83 (1H, s, CH=C(CN)₂); 7.93 (2H, d,** *J* **= 9.3, H-2,6 C₆H₄); 7.96 (2H, d,** *J* **= 9.6, H-3,5 C₆H₄); 8.14 (2H, d,** *J* **= 8.3, H-4,5 Cz). Found, %: C 77.70; H 3.70; N 10.41; S 8.02. C₂₆H₁₅N₃S. Calculated, %: C 77.78; H 3.77; N 10.47; S 7.99.**

2-({5'-[4-(9*H***-Carbazol-9-yl)phenyl]-2,2'-bithiophen-5-yl}methylidene)malononitrile (13)**. Yield 1.28 g (53%), thick orange-red mass. IR spectrum, v, cm⁻¹: 2216 (C=N). UV spectrum, λ_{max} , nm (log ε): 295 (4.20), 329 (4.08), 342 (4.05), 450 (4.54). Fluorescence spectrum, λ_{max} , nm: 599. ¹H NMR spectrum, δ , ppm (*J*, Hz): 7.19 (1H, d, *J* = 4.3, H-4' Th); 7.25 (2H, d, *J* = 9.6, H-3.6 Cz); 7.31 (2H, d, *J* = 9.0, H-1.8 Cz); 7.33 (1H, d, *J* = 4.0, H-3' Th); 7.41 (1H, d, J = 4.3, H-4 Th); 7.45 (2H, d, J = 9.0, H-2,7 Cz); 7.47 (1H, d, J = 4.6, H-3 Th); 7.63 (2H, d, J = 9.6, H-3,5 C₆H₄); 7.77 (1H, s, CH=C(CN)₂); 7.84 (2H, d, J = 9.3, H-2,6 C₆H₄); 8.15 (2H, d, J = 8.6, H-4,5 Cz). Found, %: C 74.48; H 3.50; N 8.61; S 13.20. C₃₀H₁₇N₃S₂. Calculated, %: C 74.51; H 3.54; N 8.69; S 13.26.

2-(1-{5-[4-(Diphenylamino)phenyl]thiophen-2-yl}ethylidene)malononitrile (14). Yield 0.63 g (63%), thick dark-red mass. IR spectrum, v, cm⁻¹: 2206 (C=N). UV spectrum, λ_{max} , nm (log ε): 307 (5.00), 465 (5.21). Fluorescence spectrum, λ_{max} , nm: 611. ¹H NMR spectrum, δ , ppm (*J*, Hz): 2.67 (3H, s, CH₃); 7.04 (2H, d, *J* = 8.7, H-3,5 C₆H₄); 7.12 (2H, t, *J* = 6.6, H-4,4' Ph); 7.13 (4H, d, *J* = 8.7, H-2,2',6,6' Ph); 7.27–7.32 (4H, m, H-3,3',5,5' Ph); 7.32 (1H, d, *J* = 3.6, H-4 Th); 7.50 (2H, d, *J* = 8.7, H-2,6 C₆H₄); 8.00 (1H, d, *J* = 4.2, H-3 Th). Found, %: C 77.64; H 4.54; N 10.10; S 7.58. C₂₇H₁₉N₃S. Calculated, %: C 77.67; H 4.59; N 10.06; S 7.68.

2-(1-{5'-[4-(Diphenylamino)phenyl]-2,2'-bithiophen-5-yl}-ehylidene)malononitrile (15). Yield 0.51 g (57%), thick maroon mass. IR spectrum, v, cm⁻¹: 2224 (C=N). UV spectrum, λ_{max} , nm (log ε): 303 (5.20), 357 (5.11), 477 (5.21). Fluorescence spectrum, λ_{max} , nm: 656. ¹H NMR spectrum, δ , ppm (*J*, Hz): 2.67 (3H, s, CH₃); 6.93 (2H, d, *J* = 9.0, H-3,5 C₆H₄); 7.06 (1H, d, *J* = 3.6, H-4' Th); 7.10–7.14 (6H, m, H-2,2',4,4',6,6' Ph); 7.18 (1H, d, *J* = 4.2, H-3' Th); 7.27 (4H, t, *J* = 6.6, H-3,3',5,5' Ph); 7.32 (1H, d, *J* = 3.9, H-4 Th); 7.45 (2H, d, *J* = 8.4, H-2,6 C₆H₄); 7.96 (1H, d, *J* = 4.2, H-3 Th). Found, %: C 74.45; H 4.30; N 8.47; S 12.78. C₃₁H₂₁N₃S₂. Calculated, %: C 74.52; H 4.24; N 8.41; S 12.83.

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