

Synthesis and investigation of photophysical, NLO and thermal properties of D- π -A- π -D dyes

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ABSTRACT

A novel coumarin-thiophene based dyes containing azo and dimethine bridges with D- π -A- π -D system were synthesized and investigated their photophysical, nonlinear optical (NLO) and thermal properties. The dyes were characterized by FT-IR, ¹H-NMR, ¹³C-NMR and HRMS. The dyes include dicyanomethylene group as acceptor and different *para*-substituted alkylamines and carbazole as donor and chlorophenyl as weak acceptor. The photophysical properties of dyes were examined in various solvents with different polarities and they showed absorption in the visible region. The significant bathochromic shifts were observed in the absorption maxima with increasing the electron-donating property of substituents. The second order NLO responses of the compounds are measured by the electric field induced second harmonic (EFISH) generation method and the compounds bearing dialkylamino donor in phenyl moiety were obtained as the larger $\mu\beta$ values 1300×10^{-48} esu, 1850×10^{-48} esu, respectively, than unsubstituted derivative in phenyl ring $\mu\beta$ value 350×10^{-48} esu. The structural and electronic properties of the compounds as well as their NLO properties were studied using DFT calculation. The thermal stabilities obtaining with thermogravimetric analysis (TGA) showed that the dyes have generally a good thermal stability up to 250 °C.

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1. Introduction

Azo dyes are an important class of synthetic dyes commonly used in the textile industry, the pharmaceutical industry, the cosmetic industry and the food industry [1,2]. Especially, many dyes including the donor- π -acceptor (D- π -A) systems [2–11], which are formed by connecting electron donor and acceptor groups with the π -conjugation bridges. Aromatic compounds containing azo and dimethine chromophores provide intramolecular charge transfer (ICT) by conjugating π along the azo ($-N=N-$) and dimethine ($-\text{CH}=\text{CH}-$) bridges between acceptor and donor groups [12–18]. Therefore, azo and dimethine chromophores are very important in organic dyes chemistry.

The photophysical properties of azo dyes have increased with ICT. Recently, azo dyes containing with aromatic heterocyclic units have become an interesting field of study due to their applications

in optical data storage, NLO materials [19–24]. NLO systems play an important role not only in nonlinear optics, but also in information technology and industrial applications. Non-linear absorption of materials has potential applications in multiple photoscopic microscopy and optical limiters commonly used for the protection of human eyes and optical sensors [25–27]. These systems are also referred to as donor- π -acceptor (D- π -A) systems. One of the important heterocyclic compounds found in the structure of azo dyes having this system is coumarin. Coumarin-based compounds are present in many natural and synthetic drug structures due to their low toxicity properties. In addition to these properties, coumarins have high light stability, high quantum yields, wide Stokes shift and fluorescence [28–37].

It is known that ICT is increased by binding of acceptor groups to the 3-position of the coumarin ring, D- π -A system is formed in the compound and supports the increase of fluorescence of these groups at the same time, when the thiophene compounds are connected to the coumarin ring with good donor from the 3-position, it has been determined that the thermal stability and fluorescence

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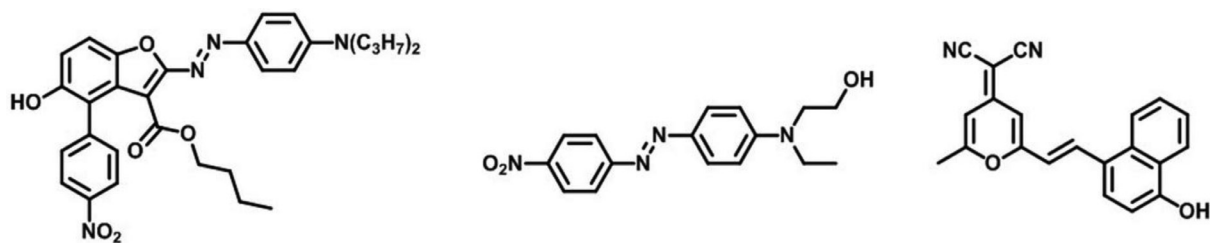


Fig. 1. NLO candidate compounds containing azo or dimethine bridge.

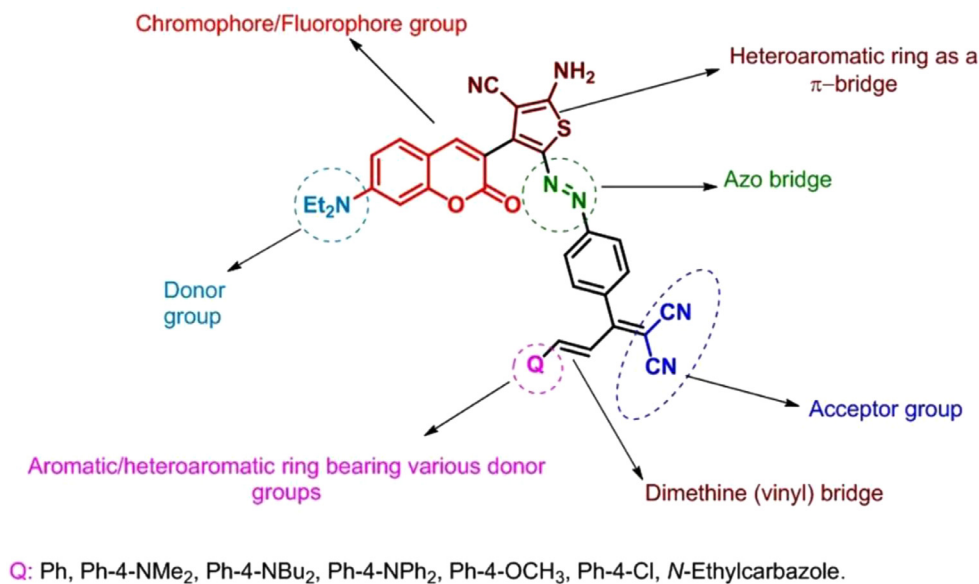


Fig. 2. Design principle of synthesized compounds.

of the compound is increased by means of ICT. Also the presence of the *N,N*-ethyl amino group as donor substituent at the 7-position of the coumarin ring supported the increase in fluorescence [38–41]. Azo and dimethine chromophores has been found to add NLO to the molecule and increase ICT.

Although many dyes including azo and dimethine bridge were designed and synthesized, synthesized dyes in this manuscript have both azo and dimethine chromophore groups in same compound which are rarely in the literature (Fig. 1). For this purpose, coumarin-thiophene hybrid system containing amino-thiophene linker, strong donor group in 7-position and cyano as acceptor group in 3-position was synthesized in present study. The target compounds were obtained via coupling reaction aminothiophenecoumarin with diazotized styryl dyes. The design principle of target dyes can be seen in Fig. 2. The structures of the new dyes having synthesized D- π -A- π -D system were confirmed by FT-IR, ¹H-NMR, ¹³C-NMR and HRMS methods. Since the presence of azo, dicyanovinyl bridge, thiophene and coumarin structures in the same molecule would contribute to the photophysical properties of the compounds. Thus, the photophysical properties of the target compounds were examined in solvents of various solvents with different polarity (DMSO, THF, DCM and ACN). The quantum chemical calculations were carried out to further insight into the experimental data. In addition, NLO properties of the compounds were determined into the framework of the calculations. Since the compounds are thought to have potential for use in optical systems, TGA have been performed to predict the thermal stability of these compounds in the application environment in optical and photonic systems.

In previous published studies, when NLO properties of structures containing dimethine chromophore and similar donor groups found in this study were examined, $\mu\beta$ values were experimentally found in the range of $120\text{--}1040 \times 10^{-48}$ esu, while in studies of coumarin-thiophene hybrid derivatives, the NLO properties of structures containing azo chromophore were only examined theoretically [41–43]. The compounds obtained in this study were synthesized more efficient and more stable compounds than those found in the literature in terms of thermal stability and NLO properties.

2. Experimental

2.1. Materials and physical measurements

All commercially available chemicals were reagent grade and used without further purification. Thin-layer chromatography (TLC) was used for monitoring the reactions using precoated silica gel 60 F₂₅₄ plates. NMR spectra were measured on Bruker Avance 300 (¹H NMR: 300 MHz, ¹³C NMR: 75 MHz) and Bruker Avance 400 (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz) spectrometers at 25 °C. Chemical shifts (δ) are given in parts per million (ppm) using the residue solvent peaks as a reference relative to TMS. Coupling constants (*J*) are given in hertz (Hz). Signals are abbreviated as follows: singlet. s; doublet. d; doublet-doublet. dd; doublet-triplet dt; triplet. t; multiplet. m. High-resolution mass (HRMS) spectra were recorded at Gazi University Faculty of Pharmacy using electron ionization (EI) mass spectrometry (Waters-LCT-Premier-XE-LTOF (TOF-MS) instruments; in *m/z* (rel.%). The melting points were measured

using Electrothermal IA9200 apparatus. Absorption spectra were recorded on a Shimadzu 1800 spectrophotometer. Thermal analyses were performed with a Shimadzu DTG-60H system, up to 700 °C (10 °C min⁻¹) under a dynamic nitrogen atmosphere (15 mL min⁻¹).

2.2. Synthetic pathway and characterization data of dyes

3-Acetyl-7-(diethylamino)-2H-chromen-2-one **1**

1 was synthesized according to the literature procedure [40].

Yield: 89%; M.p.: 152 - 153 °C (lit: 151 - 152 °C), ¹H NMR (300 MHz, DMSO-*d*₆, δ, ppm) 8.49 (s, 1H, on the Coumarin-Pyran-2-one), 7.67 (d, *J* = 9.5 Hz, 1H, Ar-H), 6.80 (dd, *J*₁ = 2.4 Hz, *J*₂ = 2.0 Hz, 1H, Ar-H), 6.58 (d, *J* = 2.3 Hz, 1H, Ar-H), 3.50 (q, *J* = 7.0 Hz 4H, -NCH₂-CH₃), 2.50 (s, 3H, -CH₃), 1.14 (t, *J* = 7.0 Hz, 6H, -NCH₂-CH₃).

2-(1-(7-(Diethylamino)-2-oxo-2H-chromen-3-yl)ethylidene) malononitrile **2**

2 was synthesized according to the literature procedure [40].

Yield: 75%; M.p.: 145 - 146 °C (lit: 145 - 146 °C), ¹H NMR (300 MHz, DMSO-*d*₆, δ, ppm) 8.33 (s, 1H, on the Coumarin-Pyran-2-one), 7.56 (d, *J* = 9.0 Hz, 1H, Ar-H), 6.83 (dd, *J*₁ = 2.3 Hz, *J*₂ = 2.3 Hz, 1H, Ar-H), 6.63 (d, *J* = 2.1 Hz 1H, Ar-H), 3.50 (q, *J* = 6.95 Hz, 4H, -NCH₂-CH₃), 2.55 (s, 3H, -CH₃), 1.15 (t, *J* = 7.0 Hz, 6H, -NCH₂-CH₃).

2-Amino-4-(7-(diethylamino)-2-oxo-2H-chromen-3-yl) thiophene-3-carbonitrile **3**

3 was synthesized according to the literature procedure [40].

Yield: 92%; M.p.: 211 - 212 °C (lit: 211 - 213 °C), ¹H NMR (300 MHz, DMSO-*d*₆, δ, ppm) 7.98 (s, 1H, on the Coumarin-Pyran-2-one), 7.48 (d, *J* = 8.9 Hz, 1H, Ar-H), 7.20 (s, 2H, -NH₂), 6.73 (dd, *J* = 2.4 Hz, 1H, Ar-H), 6.66 (s, 1H, Thiophene-H), 6.56 (d, *J* = 2.2 Hz, 1H, Ar-H), 3.45 (q, *J* = 7.69 Hz, 4H, -NCH₂-CH₃), 1.10 (t, *J* = 7.58 Hz, 6H, -NCH₂-CH₃).

2-(1-(4-Aminophenyl)ethylidene)malononitrile **4**

4 was synthesized according to the literature procedure [41].

Yield: 80%; M.p.: 185 - 186 °C (lit: 185 °C), ¹H NMR (300 MHz, DMSO-*d*₆, δ, ppm) 7.58 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.62 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.43 (s, 2H, -NH₂), 2.51 (s, 3H, -CH₃).

General Synthesis of Styryl based compounds

Styryl based compounds were synthesized according to the literature procedure [41,44].

(E)-2-(1-(4-Aminophenyl)-3-phenylallylidene)malononitrile **5a**

Dark brownish solid, Yield 57%, M.p.: 250 - 251 °C (lit: 250 - 251 °C), ¹H NMR (300 MHz, DMSO-*d*₆, δ, ppm) 7.73-7.70 (m, 2H, Ar-H), 7.50-7.47 (m, 3H, Ar-H), 7.45 (d, *J* = 15.4 Hz, 1H, vinylic-H), 7.33 (d, *J* = 8.63, 2H, Ar-H), 7.11 (d, *J* = 15.7 Hz, 1H, vinylic-H), 6.67 (d, *J* = 8.68 Hz, 2H, Ar-H), 6.22 (s, 2H, -NH₂).

(E)-2-(1-(4-Aminophenyl)-3-(4-dimethylaminophenyl) allylidene)malononitrile **5b**

Dark red solid, Yield 74%, M.p.: 216 - 217 °C (lit: 215 - 217 °C), ¹H NMR (300 MHz, DMSO-*d*₆, δ, ppm) 7.52 (d, *J* = 8.9 Hz, 2H, Ar-H), 7.21 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.17 (d, *J* = 15.1 Hz, 1H, Vinylic-H), 6.98 (d, *J* = 15.2, 1H, Vinylic-H), 6.75 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.67 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.04 (s, 2H, -NH₂), 3.00 (s, 6H, -N-CH₃).

(E)-2-(1-(4-Aminophenyl)-3-(4-dibutylaminophenyl) allylidene)malononitrile **5c**

Dark green solid, Yield 74%, M.p.: 172 - 173 °C (lit: 170 - 173 °C), ¹H NMR (300 MHz, DMSO-*d*₆, δ, ppm) 7.49 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.20 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.13 (d, *J* = 15.1 Hz, 1H, Vinylic-H), 6.95 (d, *J* = 15.1 Hz, 1H, Vinylic-H), 6.69 (d, *J* = 9.2 Hz, 2H, Ar-H), 6.68 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.00 (s, 2H, -NH₂), 1.51 (m, 4H, -NCH₂-CH₂), 1.31 (m, 4H, N(CH₂)₂-CH₂) 0.9 (t, *J* = 7.3 Hz 6H, -N(CH₂)₃-CH₃).

(E)-2-(1-(4-Aminophenyl)-3-(4-(diphenylamino)phenyl) allylidene)malononitrile **5d**

Red solid, Yield, 74%, M.p.: 205 - 206 °C (lit: 205 - 207 °C), ¹H NMR (300 MHz, DMSO-*d*₆, δ, ppm) 7.58 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.38-7.16 (m, 13H, Ar-H), 7.00 (d, *J* = 15.3 Hz, 1H, Vinylic-H), 6.87 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.67 (d, *J* = 8.5 Hz, 2H, Ar-H), 6.13 (s, 2H, -NH₂).

(E)-2-(1-(4-Aminophenyl)-3-(4-methoxyphenyl)allylidene) malononitrile **5e**

Yellow solid, Yield 77%, M.p.: 170 - 171 °C (lit: 170 - 172 °C), ¹H NMR (300 MHz, DMSO-*d*₆, δ, ppm) 7.68 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.31 (d, *J* = 15.5 Hz, 1H, Vinylic-H), 7.29 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.07 (d, *J* = 16.1 Hz, 1H, Vinylic-H), 7.01 (d, *J* = 8.9 Hz, 2H, Ar-H), 6.68 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.17 (s, 2H, -NH₂), 3.81 (s, 3H, O-CH₃).

(E)-2-(1-(4-Aminophenyl)-3-(4-chlorophenyl)allylidene) malononitrile **5f**

Dark orange solid, Yield 84%, M.p.: 207 - 208 °C (lit: 208 - 209 °C), ¹H NMR (400 MHz, DMSO-*d*₆, δ, ppm) 7.76 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.52 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.45 (d, *J* = 15.7 Hz, 1H, Vinylic-H), 7.33 (d, *J* = 8.6, 2H, Ar-H), 7.11 (d, *J* = 15.6 Hz, 1H, Vinylic-H), 6.67 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.22 (s, 2H, -NH₂).

(E)-2-(1-(4-Aminophenyl)-3-(9-ethyl-9H-carbazol-3-yl)allylidene)malononitrile **5g**

Dark reddish solid, Yield 70%, M.p.: 194 - 195 °C (lit: 193 - 198 °C), ¹H NMR (300 MHz, DMSO-*d*₆, δ, ppm) 8.54 (d, *J* = 1.0, 1H, Ar-H), 8.23 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.85 (dd, *J*₁ = 8.8 Hz, *J*₂ = 1.33 Hz, 1H, Ar-H), 7.66 (t, *J* = 8.9 Hz, 2H, Ar-H), 7.51-7.49 (m, 2H, Ar-H), 7.33-7.23 (m, 4H, Ar-H), 6.72 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.15 (s, 2H, -NH₂), 4.47 (q, *J* = 7.0 Hz, 2H, Carbazole-NCH₂-CH₃), 1.32 (t, *J* = 7.0 Hz, 3H, Carbazole-NCH₂-CH₃).

General Synthesis of Target Dyes

5a-g (1.0 mmol) was dissolved in hydrochloric acid (1.0 mL of conc. HCl in 2.0 mL of water) and the solution cooled to (-5) - 0 °C. Sodium nitrite solution (*c* = 0.5 M in water) was slowly added to the mixture. After 1 hour of stirring, urea (a small amount) was added to remove excess nitrous acid and used immediately for the coupling reaction. **4** (1.0 mmol) was dissolved in acetic acid/propionic acid (6 mL, 4:2, v:v) and cooled to (-5) - 0 °C and the diazonium salt solution was slowly added to the mixture of **4** while stirring. After 1 h, conc. sodium carbonate solution was added to the mixture till pH = 5 - 6. The mixture was stirred for an additional 1 h at (-5) - 0 °C. After 1 h, water was added to the mixture and the precipitate was filtered, washed with cold water, dried and recrystallized with ethanol to obtain pure compounds.

2-(E)-1-(4-(E)-(5-Amino-4-cyano-3-(7-(N,N-diethylamino)-2-oxo-2H-chromen-3-yl)thiophen-2-yl)diazanyl)phenyl)-3-phenylallylidene)malononitrile **6a**

Red solid, Yield: 60%, M.p.: 255 - 256 °C, FT-IR (KBr, ν_{max}, cm⁻¹): 3298, 3191, 2972, 2218, 1705, ¹H NMR (400 MHz, DMSO-*d*₆, δ, ppm) 8.78 (s, 2H, Ar-H), 8.20 (s, 1H, on the Coumarin-Pyran-2-one), 7.71 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.60 (dd, *J*₁ = 8.6 Hz, *J*₂ = 8.5 Hz, 3H, Ar-H), 7.50 (d, *J* = 15.2 Hz, 1H, Vinylic-H), 7.47 (m, 4H, Ar-H), 7.00 (d, *J* = 15.2 Hz, 1H, Vinylic-H), 6.79 (d, *J* = 3.5 Hz, 1H, Ar-H), 6.75 (d, *J* = 3.5 Hz, 1H, Ar-H), 6.61 (s, 1H, Thiophene-H), 3.47 (q, *J* = 6.5 Hz, 4H, -NCH₂-CH₃), 1.14 (t, *J* = 6.7 Hz, 6H, -NCH₂-CH₃), ¹³C NMR (100 MHz, DMSO-*d*₆, δ, ppm) 170.3, 167.6, 162.3, 158.8, 156.5, 153.2, 152.9, 151.4, 150.3, 146.7, 143.3, 138.0, 134.0, 132.0, 130.5, 130.4, 121.7, 121.5, 117.5, 115, 114.5, 114.2, 112.0, 110.6, 109.6, 107.5, 96.2, 88.5, 74.4, 44.2, 12.3, HRMS (*m/z*), (*M* + *H*)⁺: C₃₆H₂₈N₇O₂S, found: 622.2027; calc: 622.2025.

2-(E)-1-(4-(E)-(5-Amino-4-cyano-3-(7-(N,N-diethylamino)-2-oxo-2H-chromen-3-yl)thiophene-2-yl)diazanyl)phenyl)-3-(4-(dimethylamino)phenyl)allylidene)malononitrile **6b**

Bright Red solid, Yield: 58%, M.p.: 263 - 264 °C, FT-IR (KBr, ν_{max}, cm⁻¹): 3305, 3195, 2972, 2203, 1703, ¹H NMR (400 MHz, DMSO-*d*₆, δ, ppm) 8.78 (s, 2H, Ar-H), 8.20 (s, 1H, on the Coumarin-

Pyran-2-one), 7.69 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.60 (d, $J = 8.4$ Hz, 1H, Ar-H), 7.58 (m, 4H, Ar-H), 7.25 (d, $J = 15.1$ Hz, 1H, Vinylic-H), 6.86 (d, $J = 15.1$ Hz, 1H, Vinylic-H), 6.78 (d, $J = 8.4$ Hz, 1H, Ar-H), 6.73 (d, $J = 8.8$ Hz, 2H, Ar-H), 6.62 (s, 1H, Thiophene-H), 3.48 (q, $J = 6.8$ Hz, 4H, $-NCH_2-CH_3$), 3.05 (t, 6H, $N-CH_3$), 1.15 (t, $J = 6.8$ Hz, 6H, $-NCH_2-CH_3$), ^{13}C NMR (100 MHz, DMSO- d_6 , δ , ppm) 170.3, 167.6, 162.2, 158.8, 156.5, 153.2, 152.9, 151.4, 150.3, 146.7, 143.3, 138.0, 133.7, 131.6, 130.4, 121.6, 117.5, 115.0, 114.3, 112.0, 110.6, 109.6, 107.5, 96.2, 88.5, 74.4, 45.7, 44.2, 35.7, 30.7, 12.3, HRMS (m/z), ($M + H$) $^+$: $C_{38}H_{33}N_8O_2S$, found: 665.2419; calc: 665.2447.

2-(E)-1-(4-(E)-(5-Amino-4-cyano-3-(7-(N,N-diethylamino)-2-oxo-2H-chromen-3-yl)thiophene-2-yl)diazenyl)phenyl-3-(4-(dibutylamino)phenyl)allylidene)malononitrile **6c**

Dark brown solid, Yield: 58%, M.p.: 270 - 271 °C, FT-IR (KBr, ν_{maks} , cm^{-1}): 3312, 2928, 2868, 2210, 1713, ^1H NMR (400 MHz, DMSO- d_6 , δ , ppm) 7.92 (s, 1H, on the Coumarin-Pyran-2-one), 7.77 (d, $J = 8.8$ Hz, 2H, Ar-H), 7.59 (d, $J = 8.3$ Hz, 1H, Ar-H), 7.40 (m, 5H), 6.87 (d, $J = 15.2$ Hz, 1H, Vinylic-H), 6.79 (d, $J = 15.2$ Hz, 1H, Vinylic-H), 6.67 (d, $J = 2.7$ Hz, 1H, Ar-H), 6.62 (d, $J = 8.3$ Hz, 1H, Ar-H), 6.57 (d, $J = 8.8$ Hz, 2H, Ar-H), 5.70 (t, 1H, Thiophene-H), 3.47 (q, $J = 7.0$ Hz, 4H, $-N-CH_2$), 3.35 (t, $J = 8.3$ Hz, 6H), 1.37 (q, $J = 7.4$ Hz, 4H, $N-CH_2$), 1.25 (t, $J = 8.7$ Hz, 6H, NCH_2-CH_3), 0.98 (m, 8H), ^{13}C NMR (100 MHz, DMSO- d_6 , δ , ppm) 170.2, 165.3, 159.7, 156.6, 151, 149.7, 146.2, 140.6, 140.3, 134.4, 131.3, 130.4, 129.5, 122.2, 121.1, 114.4, 113.8, 111.2, 109.0, 108.0, 97.0, 50.4, 45.0, 29.0, 20.0, 13.4, 12.0, HRMS (m/z), ($M + H$) $^+$: $C_{44}H_{45}N_8O_2S$, found: 749.3411; calc: 749.3386.

2-(E)-1-(4-(E)-(5-Amino-4-cyano-3-(7-(N,N-diethylamino)-2-oxo-2H-chromen-3-yl)thiophene-2-yl)diazenyl)phenyl-3-(4-(diphenylamino)phenyl)allylidene)malononitrile **6d**

Red solid, Yield: 74%, M.p.: 321 - 322 °C, FT-IR (KBr, ν_{maks} , cm^{-1}): 3455, 3360, 2972, 2216, 1697, ^1H NMR (400 MHz, DMSO- d_6 , δ , ppm) 8.00 (s, 1H, on the Coumarin-Pyran-2-one), 7.63 (d, $J = 8.6$ Hz, 2H, Ar-H), 7.52 (d, $J = 8.9$ Hz, 1H, Ar-H), 7.45 (t, $J = 8$ Hz, 4H, Ar-H), 7.32 (t, $J = 8.7$ Hz, 4H, Ar-H), 7.25 (dd, $J_1 = 12.0$ Hz, $J_2 = 7.4$ Hz, 4H, Ar-H), 7.17 (d, $J = 8.9$ Hz, 1H, Ar-H), 7.00 (d, $J = 15.4$ Hz, 1H, Vinylic-H), 6.92 (d, $J = 8.6$ Hz, 2H, Ar-H), 6.78 (d, $J = 10.2$ Hz, 1H, Ar-H), 6.72 (d, $J = 8.6$ Hz, 2H, Ar-H), 6.61 (s, 1H, Thiophene-H), 6.20 (s, 2H, Ar-H), 3.47 (q, $J = 7$ Hz, 4H, $-NCH_2-CH_3$), 1.18 (t, $J = 7$ Hz, 6H, $-NCH_2-CH_3$), ^{13}C NMR (100 MHz, DMSO- d_6 , δ , ppm) 171.4, 165.6, 160.1, 156.5, 153.5, 151.0, 150.6, 148.3, 146.3, 141.4, 133.0, 132.5, 130.9, 130.3, 130.1, 127.5, 126.1, 125.3, 122.1, 120.5, 119.9, 116.7, 116.4, 115.5, 109.7, 108.1, 96.6, 84.5, 73.1, 44.5, 12.7, HRMS (m/z), ($M + H$) $^+$: $C_{48}H_{37}N_8O_2S$, found: 789.2776; calc: 789.2760.

2-(E)-1-(4-(E)-(5-Amino-4-cyano-3-(7-(N,N-diethylamino)-2-oxo-2H-chromen-3-yl)thiophene-2-yl)diazenyl)phenyl-3-(4-(methoxyphenyl)allylidene) malononitrile **6e**

Dark red solid, Yield: 74%, M.p.: 282 - 283 °C, FT-IR (KBr, ν_{maks} , cm^{-1}): 3314, 3219, 2977, 2210, 1711, 1493, ^1H NMR (400 MHz, DMSO- d_6 , δ , ppm) 8.78 (s, 2H, Ar-H), 8.20 (s, 1H, on the Coumarin-Pyran-2-one), 7.69 (d, $J = 7.3$ Hz, 3H, Ar-H), 7.58 (m, 3H, Ar-H), 7.42 (d, $J = 15.4$ Hz, 1H, Vinylic-H), 7.10 (d, $J = 8.3$ Hz, 2H, Ar-H), 6.96 (d, $J = 15.4$ Hz, 1H, Vinylic-H), 6.78 (d, $J = 8.8$ Hz, 2H, Ar-H), 6.62 (s, 1H, Thiophene-H), 3.80 (s, 3H, $O-CH_3$), 3.47 (q, $J = 6.6$ Hz, 4H, $-NCH_2-CH_3$), 1.15 (t, $J = 6.6$ Hz, 6H, $-NCH_2-CH_3$), ^{13}C NMR (100 MHz, DMSO- d_6 , δ , ppm) 171.0, 168.2, 162.8, 159.3, 157.0, 154.0, 152.0, 149.5, 147.3, 144.0, 138.5, 133.6, 131.7, 131.0, 127.4, 122.3, 115.3, 114.7, 113.9, 111.1, 110.1, 108.0, 96.8, 89.1, 79.5, 60.2, 56.0, 44.7, 31.2, 21.2, 12.8, HRMS (m/z), ($M + H$) $^+$: $C_{37}H_{30}N_7O_3S$, found: 652.2087; calc: 652.2131.

2-(E)-1-(4-(E)-(5-Amino-4-cyano-3-(7-(N,N-diethylamino)-2-oxo-2H-chromen-3-yl)thiophene-2-yl) diazenyl)phenyl-3-(4-(chlorophenyl)allylidene) malononitrile **6f**

Dark red solid, Yield: 65%, M.p.: 292 - 293 °C, FT-IR (KBr, ν_{maks} , cm^{-1}): 3303, 2973, 2215, 1713, ^1H NMR (400 MHz, DMSO- d_6 , δ ,

ppm) 8.78 (s, 2H), 8.20 (s, 1H, on the Coumarin-Pyran-2-one), 7.76 (d, $J = 8.6$ Hz, 2H, Ar-H), 7.73 (d, $J = 8.5$ Hz, 2H, Ar-H), 7.70 (d, $J = 15.7$ Hz, 1H, Vinylic-H), 7.55 (m, 5H, Ar-H), 6.98 (d, $J = 15.7$ Hz, 1H, Vinylic-H), 6.79 (d, $J = 3.2$ Hz, 1H), 6.62 (d, $J = 2.2$ Hz, 1H, Ar-H), 3.48 (q, $J = 5.3$ Hz, 4H, $-NCH_2-CH_3$), 1.13 (t, $J = 5.3$ Hz, 6H, $-NCH_2-CH_3$), ^{13}C NMR (100 MHz, DMSO- d_6 , δ , ppm) 162.3, 158.8, 156.5, 153.2, 152.9, 151.4, 150.3, 146.7, 143.3, 138.0, 134.0, 132.0, 130.5, 130.4, 121.7, 121.5, 117.5, 115.0, 114.5, 114.2, 112.0, 110.6, 109.6, 107.5, 96.2, 88.5, 74.4, 44.2, 12.3, HRMS (m/z), ($M + H$) $^+$: $C_{36}H_{27}N_7O_2S$, found: 656.1628; calc: 656.1635.

2-(E)-1-(4-(E)-(5-Amino-4-cyano-3-(7-(N,N-diethylamino)-2-oxo-2H-chromen-3-yl) thiophene-2-yl) diazenyl) phenyl-3-(9-ethyl-9H-carbazol-3-yl) allylidene) malononitrile **6g**

Brown solid, Yield: 57%, M.p.: 295 - 296 °C, FT-IR (KBr, ν_{maks} , cm^{-1}): 3312, 2973, 2214, 1711, 1131, ^1H NMR (400 MHz, DMSO- d_6 , δ , ppm) 8.75 (s, 1H, on the Coumarin-Pyran-2-one), 8.56 (s, 2H, Ar-H), 8.23 (d, $J = 8$ Hz, 1H, Ar-H), 7.87 (d, $J = 8$ Hz, 1H, Ar-H), 7.68 (m, 4H, Ar-H), 7.50 (t, $J = 8.8$ Hz, 1H, Ar-H), 7.32 (m, 4H, Ar-H), 7.28 (d, $J = 7.2$ Hz, 1H, Ar-H), 7.20 (d, $J = 15.0$ Hz, 1H, Vinylic-H), 7.18 (d, $J = 15.0$ Hz, 1H, Vinylic-H), 6.70 (d, $J = 8.5$ Hz, 1H, Ar-H), 6.15 (s, 1H, Thiophene-H), 4.47 (q, $J = 7$ Hz, 2H, Carbazole- NCH_2-CH_3), 3.47 (q, $J = 7$ Hz, 4H, $-NCH_2-CH_3$), 1.32 (t, $J = 7$ Hz, 6H, $-NCH_2-CH_3$), 1.12 (t, $J = 7$ Hz, 3H, Carbazole- NCH_2-CH_3), ^{13}C NMR (100 MHz, DMSO- d_6 , δ , ppm) 171.4, 167.8, 165.2, 158.8, 153.0, 150.0, 141.4, 140.1, 132.0, 126.5, 126.1, 125.6, 123.1, 122.8, 122.2, 121.3, 120.9, 119.8, 119.6, 116.0, 115.1, 113.0, 110.0, 109.7, 72.6, 44.1, 37.9, 13.7, 12.3, HRMS (m/z), ($M + H$) $^+$: $C_{44}H_{35}N_8O_2S$, found: 739.2574; calc: 739.2604.

2.3. The structure analyses of compounds

Methods in the literature were followed to obtain the starting compounds and the obtained products were confirmed by spectroscopic methods. In the ^1H NMR spectrum of **1**, the aromatic hydrogens of the benzene ring in the structure were observed as peaks between $\delta = 7.67$ ppm - 6.58 ppm and the hydrogen of the pyran-2-one ring at $\delta = 8.49$ ppm. The hydrogens of the aliphatic parts were observed between $\delta = 3.50$ - 1.14 ppm. Observation of the hydrogen of the pyran ring and the methyl hydrogens of the acetyl group at $\delta = 2.50$ ppm as singlet indicates that the desired structure has been obtained. For **2** and **3**, aromatic and aliphatic hydrogens have similar shift values. In the **2**, methyl group hydrogens shifted to $\delta = 2.55$ ppm and pyran-2-one group hydrogens to $\delta = 8.33$ ppm. This is because there is a more electron-withdrawing group in the structure than the carbonyl group. In **3**, the disappearance of methyl group hydrogens and the appearance of the hydrogen peak of the thiophene ring at $\delta = 6.66$ ppm show that the desired structures were obtained. Due to the presence of thiophene ring in **3**, the hydrogen of the pyran-2-one ring shifted to $\delta = 7.98$ ppm. The melting points of the compounds obtained in the synthesis steps of the coumarin-thiophene hybrid compound are compatible with the values in the literature, indicating that the compounds are obtained pure.

In the ^1H -NMR spectrum of **4**, aromatic hydrogens of the benzene ring were seen as doublets at $\delta = 7.58$ ppm and $\delta = 6.62$ ppm. Hydrogens of the amine and methyl groups in the structure were seen as singlets at $\delta = 6.43$ ppm and $\delta = 2.51$ ppm, respectively. Styryl compounds (**5a-g**) with dimethine chromophore generally have shifts between $\delta = 7.45$ ppm and $\delta = 6.59$ ppm in the ^1H -NMR spectrum, and vinylic hydrogens with a coupling constant of $J = 15.1$ Hz to $J = 16.1$ Hz show that the condensation reaction takes place and the compounds obtained are *E* stereoisomers. In Styryl compounds, the hydrogens of the amine group were observed as singlets between $\delta = 6.22$ - 6.00 ppm. The aromatic hydrogens of the second benzene ring added to the structure have shifts between $\delta = 7.52$ - 6.69 ppm.

In the ^1H -NMR spectra, the peaks seen in $\delta = 1.51 - 1.31$ ppm for **5b**, $\delta = 3.00$ ppm singlet for **5c**, 3.81 ppm singlet for **5e**, $\delta = 4.47$ ppm and $\delta = 1.32$ ppm for **5g** show the aliphatic hydrogens in the structures. The melting points of the compounds obtained are compatible with the values in the literature.

In the ^1H -NMR spectrum of the **6a-g**, it was observed that the hydrogen seen at $\delta = 6.66$ ppm belonging to the thiophene ring in the coumarin-thiophene hybrid compound shifted to between $\delta = 6.62 - 5.70$ ppm due to the intramolecular charge transfer after the azo bridge was obtained. With the establishment of the D- π -A- π -D system, the aromatic hydrogens in the donor groups have shifted towards the downfield. In particular, the hydrogen peak of the pyran ring has shifted to the range of $\delta = 8.75 - 7.92$ ppm. The peak number obtained in the ^{13}C -NMR spectrum is compatible with the carbon numbers in the structures of the compounds. An increase was seen for the melting points of the **6a-g** compared to the melting points of the starting compounds. In the HRMS spectra, the molecular ion peak was found with the difference between the calculated mass (-6.2) - 3.3 ppm. With the characterization methods, it is supported that the target compounds are in the desired structure.

2.4. Computational details

The geometry optimizations were done by using Density Functional Theory (DFT) at B3LYP/6-31G(d,p) level [45,46]. The absorption spectra were calculated within the time-dependent DFT (TD-DFT). The NLO properties were also calculated at the same level. Polarizable Continuum Model (PCM) were used for the calculations in solvent [47,48]. All the calculations were done using Gaussian 09 program [49].

3. Results and discussion

3.1. Synthesis of dyes

As depicted from Scheme 1, the reaction pathway starts from diazotated of compounds **5a-g**, its reaction with compound **4** in propionic acid/acetic acid mixture through well-known coupling reaction gives compounds **6a-g** in moderate to good yields, generally without the need for chromatographic purification. General procedures regarding the synthesis of both compounds are presented in the Scheme 1. The structures of the all new synthesized compounds were confirmed by FT-IR, $^1\text{H}/^{13}\text{C}$ NMR and HRMS (Fig. S1–39 in Supporting Information). In addition, the stereochemistries of the double bonds in compounds were determined on the basis of the coupling constants of the vinylic hydrogens in the ^1H NMR spectra ($J \approx 15\text{--}16$ Hz). The results show that the compounds are stable as *E* stereoisomer.

3.1. Photophysical results

To assess the effect of the solvent on the absorption spectra of compounds **6a-g**, various solvents with different polarity were employed at room temperature (Fig. 3 and 4, Table 1, Fig. S40–51 and Table S1–6 in Supporting Information). Unfortunately, many solvents mainly less-polar or non-polar could not be used because of the limited solubility of chromophores. The shifts of the absorption maxima of these dyes are little dependent from the solvent polarity and there are small differences of absorption maxima values for all dyes. Dye **6a** has no substituent in phenyl ring therefore, it was taken as reference compound while evaluating solvents and substituents effects. As representative examples, the spectra of **6a** is provided in Figs. 3 and 4. The absorption max-

imum wavelengths and molar absorption coefficients of the synthesized compounds were calculated in the solvents in which they were dissolved. Absorption spectra were taken in 10 μM solutions. In all cases, a significant red shift in the absorption maximum of all dyes in DMSO was observed in comparison to the other solvents such as ACN, THF and DCM. All the dyes except **6d** and **6g** showed a main peak with a shoulder. The observed shorter absorption wavelength band in the range of 365–435 nm is mainly due to $\pi\text{--}\pi^*$ transition of the aromatic/heteroaromatic ring and the other longer absorption wavelength band in the range of 467–540 nm is due to $n\text{--}\pi^*$ (charge transfer from donor to acceptor) respectively. However, dye **6d** display two strong maxima with almost same intensity because of having larger aromatic surfaces than others. In addition, **6g** have large absorption band in the range of 400–500 nm. The dye **6b** which has bearing the strongest electron donating substituent, shows red-shifted absorption, as compared to the other six dyes (Fig. 3, Table 1, Fig. S40–45, Supporting Information). Interestingly, absorption maxima values and shape of absorption peak of chloro substituted derivative **6f** and unsubstituted derivative **6a** are almost same. In addition, it was obtained color of dyes in solvents used and the results showed that the compounds have generally yellow color and color shift to red with increasing of donor strength of substituents (Fig. 4). The calculated absorption maxima of **6a-g** with using the TD-DFT calculations performed on the ground state geometry of each compound (Fig. 5) are consistent with experimental one (Table 1 and Table S1–S6, in Supporting Information).

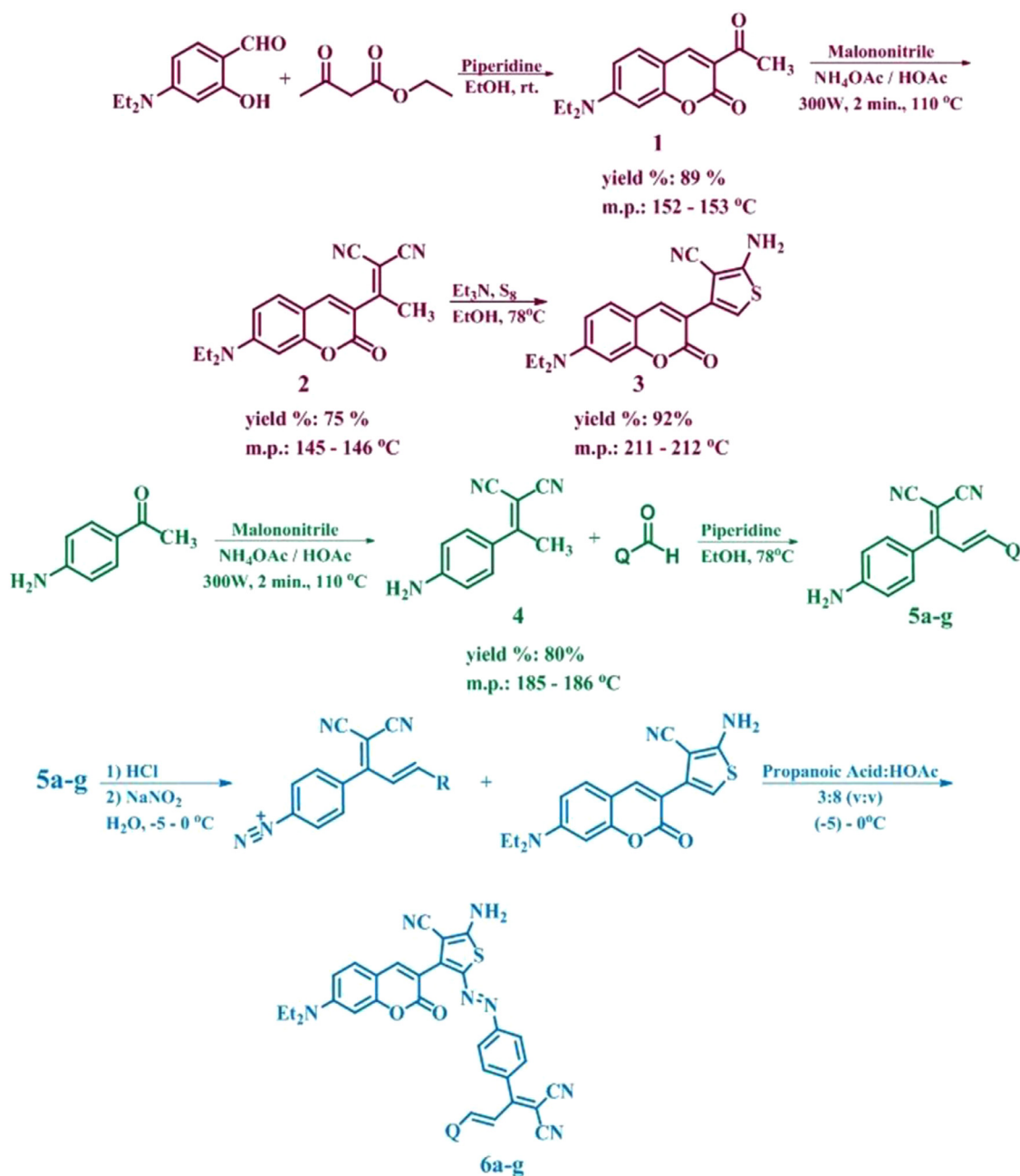
3.2. NLO properties

The second-order NLO responses of all dyes were measured by the EFISH technique in CHCl_3 solution with a non-resonant incident wavelength of 1907 nm. Experimental details on EFISH measurements are given elsewhere [50]. EFISH measurements provide information about the scalar product $\mu\beta(2\omega)$ of the vector component of the first hyperpolarisability tensor β and the dipole moment vector [51–54]. This product is derived according to Eq. (1) and considering $\gamma_0(-2\omega, \omega, \omega, 0)$, the third-order term, as negligible for the push-pull compounds under consideration. This approximation is usually used for push-pull organic and organometallic molecules.

$$\gamma_{\text{EFISH}} = \mu\beta/5kT + \gamma_0(-2\omega, \omega, \omega, 0) \quad (1)$$

The results of EFISH measurements are presented in Table 2. The solubility of **6d** was very low in CHCl_3 for obtaining correct value, therefore the EFISH value of **6a** cannot be presented in here. The obtained positive $\mu\beta$ values indicate that excited states are more polarized than the ground state and that both ground and excited states are polarized in the same direction for **6a-c** and **6e-g**. The studied compounds exhibited a higher NLO response than Disperse Red 1 generally used as a reference ($\mu\beta = 450 \times 10^{-48}$ esu).

As consistent with the photophysical properties, when the strength of donor groups bearing of phenyl ring increase, the $\mu\beta$ values are found to increase. The unsubstituted derivative **6a** and chloro substituted derivative **6f** exhibit the same order NLO response. **6b**, **6c**, **6e** and **6g** exhibit the higher NLO response as compared to unsubstituted derivative **6a** and chloro substituted derivative **6f**. The calculated μ , β and $\mu\beta$ values from the DFT calculations at B3LYP/6-31G(d,p) level in CHCl_3 are also given in Table 2. In the calculations, the trend in experimental results for $\mu\beta$ values that increases from **6a** to donor group substituted derivatives were obtained. However, the individual changes of μ and β were different as given in Table 2. When compared with similar studies and compounds in the literature, the D- π -A- π -D sys-



Q: Ph (5a, 6a), Ph-4-NMe₂ (5b, 6b), Ph-4-NBu₂ (5c, 6c), Ph-4-NPh₂ (5d, 6d), Ph-4-OCH₃ (5e, 6e), Ph-4-Cl (5f, 6f), *N*-Ethylcarbazole (5g, 6g)

Scheme 1. Synthetic pathway of compounds 6a-g.

tem was established and the NLO properties were improved by using dimethine and azo chromophores in the same compound [41–43].

3.3. TGA results

Thermal stability is quite important for NLO chromophore while using as electrooptic material. Therefore, we conducted TGA to understand whether the molecule is sufficient for NLO study. NLO candidate chromophores must be thermally stable (> 200 °C) and they should have high thermal dissociation value enough to apply

in electric field poling [55]. As depicted from Fig. 6, mass wise all compounds show non-complete dissociation under inert environment up to 600 °C. All compounds showed zero weight loss up from 0 up to 100 °C except 6a thus indicates that there is no water or other volatile organic solvents residue on the surface of all compounds. Compounds **6b**, **6e** and **6f** were found to be stable up to 250 °C, and **6c**, **6d** and **6g** were found stable up to 280 °C. The thermal stability of 6a is lower than other compounds. If the substituent is attaching to phenyl ring, thermal stability of compounds increase. NLO devices operate at high temperatures and it is very important that compounds to be used in NLO applications remain

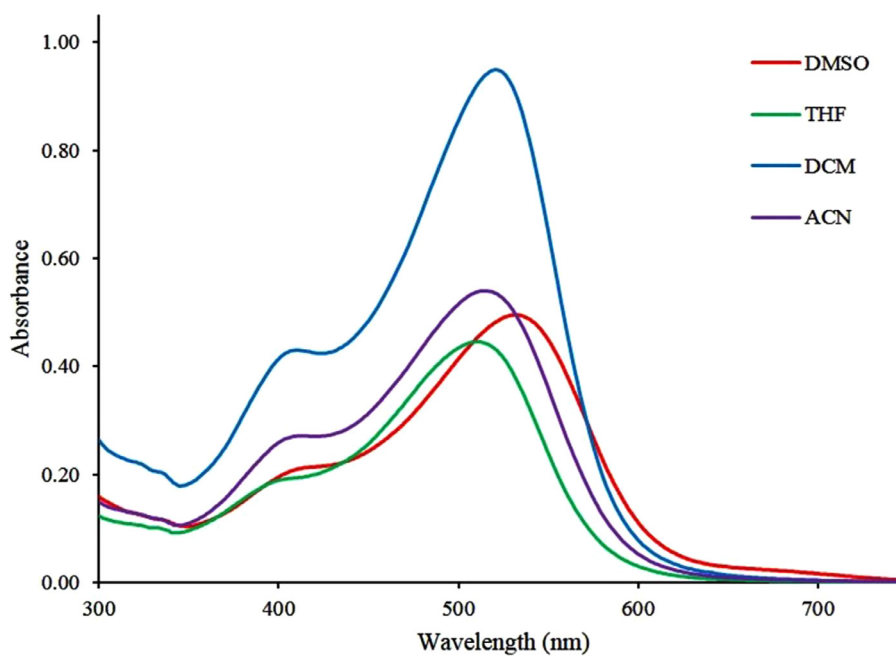


Fig. 3. UV-vis spectrum of dye **6b** ($c = 10 \mu\text{M}$) in various solvents.

Table 1

The experimental and calculated spectra data for **6b** in various solvents.

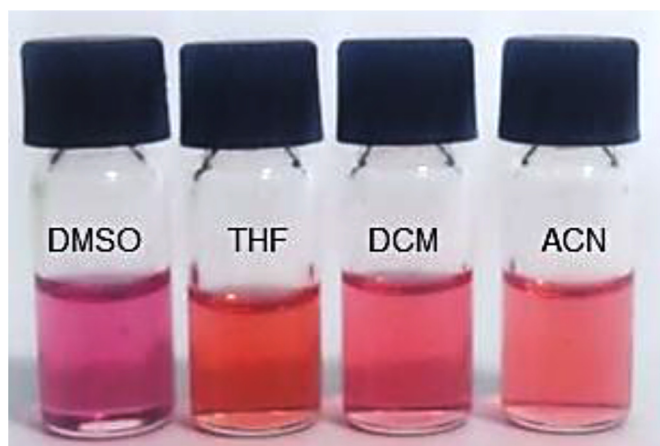
Solvent	λ_{max} (nm) ^a	ε (cm ⁻¹ M ⁻¹) ^a	λ_{max} (nm) ^b	f^b	Transition ^b	w(%) ^b
DMSO	410 ^s ,514	54,320	373	0.7463	HOMO-5→LUMO	2.6
					HOMO-2→LUMO	2.4
					HOMO-2→LUMO+1	5.1
					HOMO-2→LUMO+2	3.5
					HOMO-1→LUMO+2	54.1
			490	0.5254	HOMO→LUMO+2	29.2
					HOMO-3→LUMO	5.4
					HOMO-2→LUMO	68.8
					HOMO→LUMO+1	20.7
					HOMO-5→LUMO	3.1
ACN	408 ^s ,496	64,209	371	0.7326	HOMO-5→LUMO	2.6
					HOMO-2→LUMO	5.3
					HOMO-2→LUMO+1	3.8
					HOMO-2→LUMO+2	51.1
					HOMO-1→LUMO+2	30.9
			488	0.5064	HOMO→LUMO+2	5.7
					HOMO-3→LUMO	68.3
					HOMO-2→LUMO	20.6
					HOMO→LUMO+1	3.5
					HOMO-5→LUMO	2.2
DCM	410 ^s ,498	94,675	371	0.7371	HOMO-2→LUMO	4.6
					HOMO-2→LUMO+1	3.7
					HOMO-2→LUMO+2	24.3
					HOMO-1→LUMO+2	58.8
					HOMO→LUMO+2	6.4
			489	0.4939	HOMO-3→LUMO	69.4
					HOMO-2→LUMO	20.3
					HOMO→LUMO+1	3.8
					HOMO-5→LUMO	2.2
					HOMO-2→LUMO	4.8
THF	410 ^s ,489	81,584	371	0.7300	HOMO-2→LUMO+1	3.8
					HOMO-2→LUMO+2	16.9
					HOMO-1→LUMO+2	65.5
					HOMO→LUMO+2	6.8
					HOMO-3→LUMO	69.3
			489	0.4828	HOMO-2→LUMO	19.5
					HOMO→LUMO+1	

s: shoulder; $c = 10 \mu\text{M}$. a: experimental data. ε : molar absorption coefficient (cm⁻¹M⁻¹) calculated by absorption maxima in long wavelength. b: TD-DFT data. f: oscillator strength. w: transition contribution. HOMO: The highest occupied molecular orbital. LUMO: The lowest unoccupied molecular orbital.

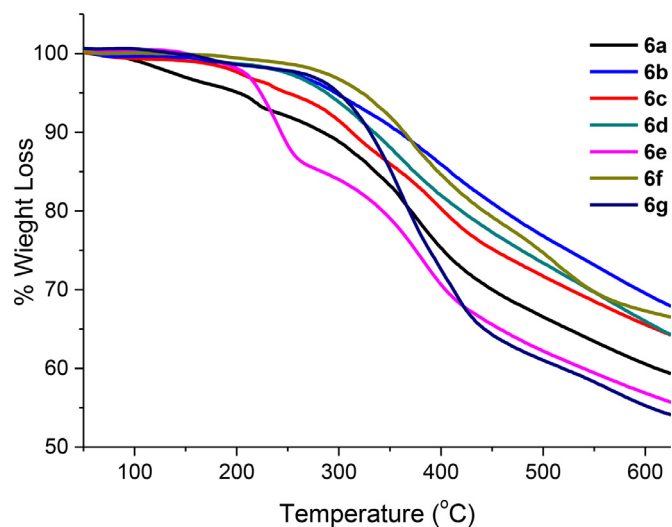
Table 2
 $\mu\beta$ values for **6a-c** and **6e-g**.

	μ^a (Debye)	$\beta^a (\times 10^{-30})$ (esu)	$\mu\beta^a (\times 10^{-48})$ (esu)	$\mu\beta^b (\times 10^{-48})$ (esu)
6a	3.13	418	1308	350
6b	9.96	222	2211	1300
6c	10.66	249	2654	1850
6e	5.42	305	1653	600
6f	1.04	429	446	400
6g	7.87	218	1715	1000

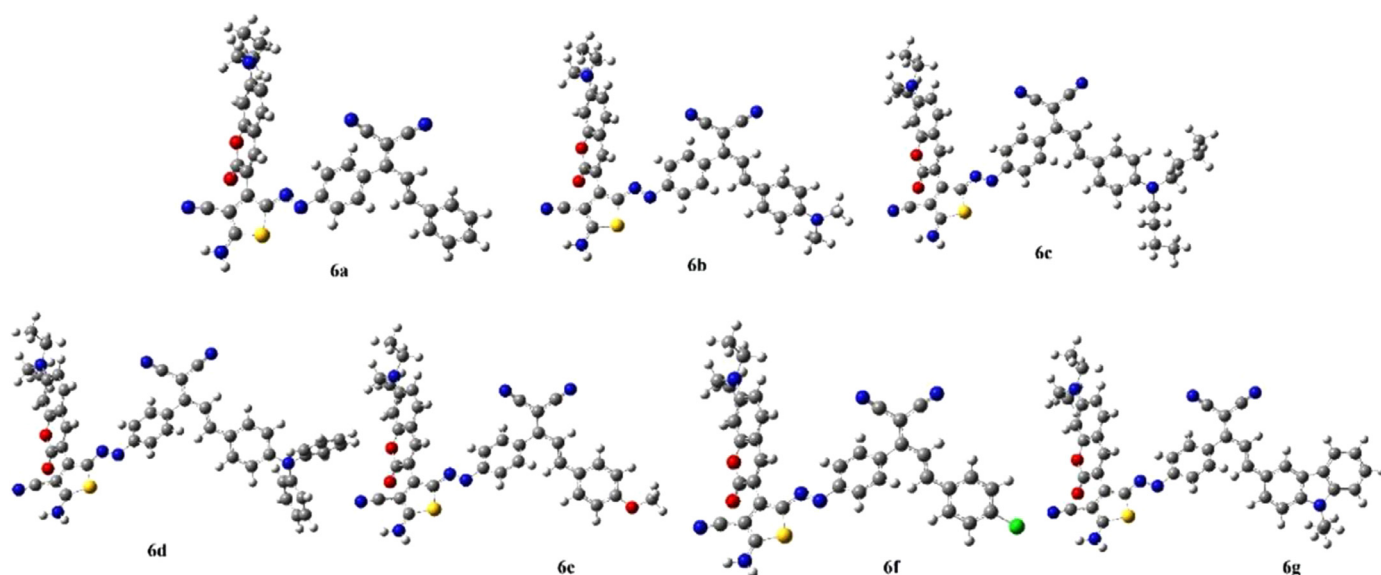
^a DFT results at B3LYP/6-31G(d,p) level in CHCl_3 . ^b EFISH: $\mu\beta$ (2ω) at 1907 nm in CHCl_3 , molecular concentrations used for the measurements were in the range of 10^{-3} to 10^{-2} M, $\mu\beta \pm 10\%$.

**Fig. 4.** Photograph of **6b** in various solvents under ambient light.**Table 3**
 T_d values of **6a-g**.

Compounds	T_d (°C)
6a	108
6b	286
6c	310
6d	256
6e	287
6f	312
6g	315

**Fig. 6.** TGA curves of **6a-g**.

thermally stable at high temperatures. The thermal stability of similar compounds in previously published studies is generally around up to 315 °C for coumarin-thiophene hybrid compounds, while it is around up to 266 °C for compounds with donor groups similar to the groups in this study containing the dimethine chromophore [35,36,41,42]. According to results, the dyes except **6a** have high potential for use in optical systems since the T_d values of the synthesized compounds are above 250 °C (Fig. 6 and Table 3).

**Fig. 5.** The optimized structures of **6a-g**.

4. Conclusions

In summary, we have successfully synthesized a series of seven novel D- π -A- π -D type push-pull dyes including free amine, azo and dimethine bridge in same structure. The structures of synthesized compounds were determined by ^1H NMR, ^{13}C NMR, HRMS, FT-IR methods. Since the presence of azo, dicyanovinyl bridge, thiophene and coumarin structures in the same molecule would contribute to the photophysical properties of the compounds and their photophysical properties were investigated in solvents of various polarity. The increase in electron transfer from the donor to the acceptor in the molecule also contributed to the bathochromic shift. It was found that the synthesized compounds have a good NLO response with high thermal stability for potential using in optical systems.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Arda Özarslan: Conceptualization, Investigation. **Deniz Çakmaz:** Conceptualization, Investigation. **Fatma Erol:** Conceptualization, Investigation, Writing - original draft. **Hülya Şenöz:** Writing - review & editing. **Nurgül Seferoğlu:** Conceptualization, Software, Writing - review & editing. **Alberto Barsella:** Conceptualization, Methodology. **Zeynel Seferoğlu:** Conceptualization, Methodology, Writing - review & editing.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2020.129583.

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