

Month 2019 Discovery of Novel D-A and D-π-A Structured Carbazole-Based Formazan Dyes: Synthesis, Characterization, and Spectroscopic Studies

Cevher Gundogdu Hizliates* 问

Department of Chemistry, Faculty of Sciences, Dokuz Eylul University, Tınaztepe Campus, 35160 Buca, Izmir, Turkey *E-mail: cevher.gundogdu@deu.edu.tr

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In the current study, new carbazole-based formazan dyes, D-A and D- π -A, were synthesized, and their spectroscopic properties were studied for the first time. For this aim, carbazole aldehyde compounds were modified by the derivatization of carbazole, a natural electron-donor compound, from 3- and 9-position. Then, hydrazone derivatives were synthesized from these aldehyde derivatives. Finally, D-A (**5A–C**) and D- π -A (**6A–C**) carbazole–formazan dyes were obtained by the interaction of the hydrazone compounds with *p*-substituted aniline. After characterization of the structures of these compounds, photophysical properties of the carbazole–formazans were studied in the different polarity media (i.e., acetonitrile, toluene, and chloroform) in order to detect the solvent effects. Because of the π -conjugated bridge and the electron acceptor nitro group at the para position, D- π -A structured carbazole–formazan dye **6C** showed the highest Stokes shift of 155 nm.

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INTRODUCTION

In recent days, design and development of second-order nonlinear optical materials and two light-emitting molecules that have high polarity and thermal stability, good optical transparency in the visible region, good compliance with high-performance polymer, and excellent resolution are gaining importance with the increasing use of two-photon technology in optoelectronics, photonics, organic light-emitting diodes, optical power limiting, photodynamic therapy, singlet oxygen production, the three-dimensional micro-manufacturing, and storage of data and three-dimensional fluorescence microscopy [1–3].

Organic π -conjugated molecules, which have both electron donor (D) and electron acceptor group (A), exhibit interesting optical and spectral properties with an intramolecular charge transfer from acceptor group to the donor. In these fluorophore molecules, the typical embodiment is D- π -A form. It is determined that the molecules that are designed by the binding of different donor and acceptor groups with optimal π -conjugated bridge show high hyperpolarization (β). This development in β ensures the redshift of the maximum absorption wavelength. These systems are often used in the nonlinear optical system, the optical data storage devices, organic light-emitting diodes, and organic-inorganic hybrid materials [4].

Because of their biological and technological properties, carbazole and formazans are very important compounds for chemists. Carbazoles are well known conjugated, good hole-transporting, electron-donor, and planar compounds [5–8]. Carbazole derivatives are important optical materials owing to their inherent electron-donating and nonlinear optical properties, hole-transporting capabilities, and high charge carrier mobilities, and high thermal and photochemical stabilities [9,10]. Therefore, these compounds are used in a wide range of electronic and photonic applications such as photo-refractive materials [11], photoconductors [12], nonlinear optical materials [13,14], hole-transporting materials [15], and organic light-emitting materials [16–20].

On the other hand, formazans have a wide application range as dyes, ligands [21,22], and analytical reagents because of their color changes in redox reactions like an indicator [23]. Formazans are colored compounds due to π - π * and n- π * transitions. Hausser et al. [24] have shown that many formazans could be obtained in red and yellow forms on exposure to visible light. Red formazan molecules have hydrogen bridge show chelate, and the yellow shows non-chelate form [25]. Formazans create complexes and salts with transition metal ions such as Zn, Co, Cu, Fe, Mn, and Pd(II) [26–32]. Formazans are easily oxidized to colorless tetrazolium salts, and tetrazolium salts are reduced back to formazans by enzymes in the cell and stain the tissue. Because of this feature, tetrazolium/formazan systems have been used as indicators in marker of vitality, in screening of anticancer drugs, and in determination of tumor cell activity and sperm viability [33–35]. Also, it is well known that formazans have antiviral, anti-inflammatory, antitubercular, and antimicrobial activities [36,37].

In the present study, we intended to design and synthesize D-A and D- π -A carbazole–formazan dyes bearing electron-donor carbazole and electron acceptor formazan moieties. After determination of their structural analysis, their basic photophysical properties were exhibited.

The substituent effects were obtained by changing the group at the para position of the phenyl ring, and the solvent effect was investigated by using different polarity solvents such as chloroform, acetonitrile, and toluene.

RESULTS AND DISCUSSION

Synthesis and structure. Herein, novel D-A (5A–C) and D- π -A (6A–C) structured carbazole-based formazan dyes were prepared to combine the advantages of carbazole and formazan moieties for the first time.

In this study, carbazole aldehyde phenylhydrazone (3, 4) was obtained by the condensation reaction of carbazole aldehyde (1, 2) and phenylhydrazine at pH 5–6. Then, carbazole-based formazans were synthesized by coupling of carbazole aldehyde phenylhydrazone (3, 4) with benzene diazonium chloride derivatives at -5° C and at pH 10–12. The synthetic route of the target compounds is presented in Scheme 1.

In the IR spectra, N–H, C=N, and N=N stretching bands are important for formazans. Shifting toward lower or higher frequency of these bands determines the chelate or non-chelate structure. For D-A derivatives, bands observed at 3422–3425, 1590–1595, 1492–1518, and 1322–1325 and, for D- π -A derivatives, at 3422–3426, 1596–1598, 1449–1450, and 1226–1233 cm⁻¹ belonged to N–H stretching, C=N stretching, N=N stretching, and C–N stretching, respectively. Because of the charge transfer from carbazole to the nitro group, **5C** and **6C** decreased the vibration band of C=N group.

The N–H signal of formazan in the NMR spectrum is indicative in evaluating the structure. When N–H signals of carbazole–formazan dyes were examined in the ¹H-NMR spectrum and the positions of their signals were compared, D-A structured compounds (**5A–C**) exhibited sharp NH signal in the upfield region at δ 8.68–8.84 ppm;

this indicated a weakening of the intramolecular hydrogen bonding. In D-π-A structured compounds (6A-C), N-H signals were observed in the downfield region at δ 15.23– 15.52 ppm, and it showed intramolecular hydrogen bonding. In formazans, 5A-C where the carbazole ring was substituted with -CH₃ group from indole nitrogen exhibited $-NCH_3$ signals at δ 3.75–3.87 ppm. Methyl hydrogens of **5B** compound appeared at δ 2.46 ppm. For 5A-C and 6A-C compounds, aromatic hydrogens were observed at their expected region. The chemical shifts of the aromatic and -NH protons were caused by the inductive and resonance effects of the type and position of the substituents. From the ¹³C-NMR values of the carbazole-formazans, it was observed that D-A structured compounds 5A and 5C gave 26C and D-n-A structured compounds 6A and 6C gave 31C peak. In compounds 5B and 6B, one more C peak was observed because of the p-CH₃ substituent. The calculated mass and founded mass obtained from HR-MS analyzes were determined as compatible with each other.

Photophysical properties of D-A and D- π -A structured carbazole–formazan derivatives. This work also describes the photophysical characterization of carbazole–formazans in different solvents with different polarities such as acetonitrile, chloroform, and toluene for the detection of solvent effect. Absorption, excitation, and emission wavelength; molar extinction coefficients (ϵ), singlet energy, Stokes's shift, and quantum yields values were recorded for 1×10^{-5} M dye solutions; and results were given in Table 1. Discussions were focused on λ_{max1} values of the carbazole–formazan derivatives, which are characteristics of the formazan structures.

The fluorescence quantum yields of the carbazole– formazan derivatives were calculated according to formula 1, and fluorescein 27 standard in 0.1M NaOH (F_{std} : 0.95) was used as the reference standard [38]:

$$\Phi_{\rm f} = \Phi_{\rm st} \left(F A_{\rm st} \cdot \eta^2 \right) / \left(F_{\rm st} A \eta^2_{\rm st} \right). \tag{1}$$

F is the area under the fluorescence emission curve; *A* is the respective absorbance value at the excitation wave-

length; and η is the refractive index of the medium solvent. The spectra of carbazole–formazans (Figs 1 and 2) exhibited three distinctive absorption bands (A, B, and C). The first band (A) in the range of 292–304 nm was observed because of the low π - π * energy transfer of the phenyl group. The second band (B) was shown at 315- to 388-nm range, which corresponded to π - π * electronic transitions of -N=N- group in the molecule.

The third broad band that was observed at 478–547 nm was characteristic of the formazan structure due to π - π * and n- π * electronic transitions in formazan skeleton.

In this study, carbazole and formazan moieties were chosen as an electron-donor group and an electron acceptor group, respectively. Also, benzene ring was used

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Scheme 1. The formation mechanism of formazans.



as a π -conjugated bridge for D- π -A compounds. On the other hand, *p*-methyl and *p*-nitro aniline derivatives were used for the synthesis of carbazole–formazans in order to observe the substituent effect.

When the UV–vis absorption spectra of the synthesized carbazole–formazan derivatives were compared, it was seen that all derivatives gave maximum absorption in the lowest-polarity solvent toluene, because the polar solvents stabilize the π^* bond and increase the wavelength by reducing the energy at the n– π^* transition. It was determined that absorption maxima of D- π -A derivatives were redshifted in comparison with D-A derivatives because of the increase of π – π^* transitions and decrease of energy.

While the D-A compounds showed excitation maxima between 414 and 441 nm and emission maxima in the 477- and 533-nm range, D- π -A compounds showed excitation maxima between 371 and 445 nm and emission maxima between 466 and 553 nm (Figs 3 and 4). In comparison with D-A and D- π -A carbazole-formazans, **6A–C** dyes, which were D- π -A structured compounds, showed bathochromic shift for emission maxima in more polar acetonitrile media, and for 5A-C dyes, a redshift was shown for fluorescence band in chloroform that is the less polar solvent used in this study. This might be due to the formation of $\pi^* - \pi$ transitions by increasing π -bonds in the D- π -A derivatives. Owing to increased conjugation at the *p*-position by the electron-withdrawing nitro group, **5**C dye gave the highest emission wavelength at 533 nm in chloroform solution and 6C dye gave the highest emission wavelength value at 553 nm in acetonitrile solution. Therefore, the substitution of electron acceptor nitro group

upon formazan molecule increased conjugation and the photosensitization, and it also caused a bathochromic effect upon emission wavelength for D-A **5C** dye in chloroform and for D- π -A **6C** dye in acetonitrile when compared with **5A** and **6A**. On the other hand, the electron-donor methyl groups decreased the conjugation and photosensitization, and they also caused a hypsochromic effect upon λ_{max} values for D-A **5B** dye in chloroform and for D- π -A **6B** dye in acetonitrile in comparison with **5A** and **6A**.

The Stokes shift values were calculated for all derivatives, and the highest values were obtained for electron acceptor nitro group substituted **5C** compound at 115 nm and for **6C** compound at 155 nm, in comparison with the values of methyl group substituted compounds **5B** and **6B** as electron acceptor. Intramolecular charge transfer increased for D- π -A carbazole–formazan dyes owing to π -conjugated bridge, and the highest Stokes shift was observed for **6C** dye. The Stokes shift values were higher in chloroform for D-A derivatives and in acetonitrile for D- π -A derivatives.

As shown in Table 1, the highest fluorescence quantum yield values were obtained in toluene. Because of the decrease in the polarity of media, some interactions can be related and the quantum yield can increase.

EXPERIMENTAL

Reagents and apparatus. All melting points were measured in sealed tubes using an electrothermal digital melting point apparatus (Gallenkamp). Fourier transform

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Table 1

Absorption and fluorescence emission and excitation data for D-A and D- π -A structured carbazole–formazan compounds (λ , nm and ϵ , L mol⁻¹ cm⁻¹), Stokes shifts, $\Delta\lambda$ (nm), singlet energy, E_s (cal mol⁻¹), and fluorescence quantum yield, ϕ , in solutions

Туре	Compound	Solvent	λ^{ab}_{max}	3	$E_{\rm s}$	λ_{max}^{em}	λ_{max}^{ex}	Δλ	φ
D-A	5A	Chloroform	485	32,100	5874	524	428	96	0.0495
			315	72,900	9048				
			293	77,100	9744				
		Toluene	499	10,900	5717	482	441	41	0.1585
			315	25,500	9048				
			294	32,400	9694				
		Acetonitrile	495	16,800	5758	523	439	84	0.0914
			318	38,900	8976				
			295	42,200	9677				
	5B	Chloroform	485	78,300	5870	515	426	89	0.0121
			340	100,700	8382				
			292	121,400	9760				
		Toluene	500	8400	5700	485	424	61	0.2674
			331	55,900	8610				
			293	84,200	9726				
		Acetonitrile	491	27,400	5804	505	425	80	0.0607
			342	174,900	8333				
		~ ~ ~	294	209,700	9710				
	5C	Chloroform	478	19,700	5962	533	418	115	0.0206
			325	31,500	8769				
			293	36,000	9727				
		Toluene	500	10,500	5706	477	420	57	0.0853
			328	22,000	8702				
			293	37,700	9727	510		0.0	0.0445
		Acetonitrile	494	13,000	5775	513	414	99	0.0417
			327	21,900	8728				
		CI I C	294	28,000	9710	471	200	01	0.0205
D- π-А	0A	Chloroform	519	25,800	5491	4/1	380	91	0.0385
		T - 1	502	109,100	9437 5240	502	445	57	0.0502
		Toluene	545 204	10,400	5249	502	445	57	0.0503
		A aatamitrila	504	21,600	9373	504	271	122	0.0146
		Acetoinune	333	21,000	0375	504	371	155	0.0140
	6 D	Chloroform	527	90,800	5207	169	275	02	0 1616
	0D	Ciliolololili	278	218 300	9927	408	515	93	0.1010
		Toluene	543	7100	5253	466	301	75	0.2112
		Toldelle	292	85 600	9760	400	571	15	0.2112
		Acetonitrile	520	8900	5481	501	380	121	0 1197
		rectonune	295	95,900	9677	501	500	121	0.1177
	60	Chloroform	504	44 900	5655	521	385	92	0.1103
	ve	Childrenon	388	74 200	7345	521	565	12	0.1105
			297	127 800	9596				
		Toluene	547	24.400	5210	490	410	80	0.1124
		1 Studio	382	41.000	7471	120	.10	50	0.1121
			301	72.500	9484				
		Acetonitrile	532	33.000	5362	553	398	155	0.0454
			388	53,600	7355				
			301	92,200	9484				
				· · · ·	-				

infrared spectroscopy analysis was studied with PerkinElmer Spectrum BX-II Model FTIR spectrophotometer. NMR spectra were recorded and obtained on Varian AS-400 NMR (Varian, Inc., Palo Alto, CA) at 400 MHz for ¹H-NMR and 100 MHz for ¹³C-NMR.

Mass spectra were determined on the electron impact mode by direct insertion at 70 eV with a Micromass UK Platform II LC-MS spectrometer. The absorption spectral data were measured by using a Shimadzu 164 UV-1601 spectrophotometer (Shimadzu Corp., Kyoto, Japan), and fluorescence measurements were recorded with Varian-Cary Eclipse Fluorescence spectrofluorometer. Analytical and preparative thin-layer chromatographies were carried out using silica gel 60 HF-254 (Merck, Kenilworth, NJ). Column chromatography was carried out by using 70–230 mesh silica gels (0.063–0.2 mm, Merck).



Figure 1. The absorption spectra of D-A structured carbazole–formazan dyes (5A–C) in (a) chloroform, (b) toluene, and (c) acetonitrile. [Color figure can be viewed at wileyonlinelibrary.com]

Reagent and conditions. (i) Phenylhydrazine, methanol, and acetic acid, reflux, 6 h. (ii) N,N-Dimethyl formamide, pyridine, aniline, HCl, NaNO₂, -5° C.

General procedure of synthesis of carbazole hydrazone derivatives. Carbazole aldehydes 1 and 2 (5 mmol) synthesized according to literature [39,40] were dissolved in methanol (50 mL) and acetic acid (1 mL), and then phenylhydrazine (5 mmol) was added with constant stirring at pH 5–6 within 30 min. The reaction mixture was refluxed for 5 h, and resulting carbazole hydrazone compound 9-methyl-3-((2-phenylhydrazono)methyl)-9*H*-carbazole (3) and 9-(4-((2-phenylhydrazono)methyl) phenyl)-9*H*-carbazole (4) were filtered and recrystallized from methanol [41,42].

9-Methyl-3-((2-phenylhydrazono)methyl)-9H-carbazole

(3). Yellow solid; yield: 1.29 g (90%); mp: 168°C; IR (KBr, cm⁻¹) v: 3442 (NH), 1597 (C=N), 1476 (N=N), 1364 (C-N). ¹H-NMR (CDCl₃, 400 MHz δ (ppm)): 3.89 (s, 3H, CH₃), 7.02–7.06 (td, 1H, ArH, J = 8.6 and 1.2 Hz), 7.07–7.19 (m, 3H, ArH, NH), 7.21–7.28

(m, 2H, ArH), 7.36–7.38 (dd, 1H, ArH, J = 8.0 and 1.6 Hz), 7.54–7.61 (m, 3H, ArH), 7.71–7.81 (m, 3H, ArH), 7.96 (s, 1H, CH=N). ¹³C-NMR (CDCl₃ 400 MHz δ (ppm)): 145.2 (C=N), 142.6 (NHC), 142.3, 141.9, 135.3, 130.0, 129.2 (2C), 127.8, 126.4, 124.8, 123.6, 123.2, 120.6, 120.2, 114.5 (2C), 109.2, 109.2, 29.3 (NCH₃).

9-(4-((2-Phenylhydrazono)methyl)phenyl)-9H-carbazole

(4). Yellow solid; yield: 0.34 g (48%); mp: 185°C; IR (KBr, cm⁻¹) v: 3314 (NH), 1599 (C=N), 1506 (N–N), 1360 (C–N). ¹H-NMR (CDCl₃, 400 MHz δ (ppm)): 6.94 (t, 1H, ArH, J = 7.2 Hz), 7.16 (d, 2H, ArH, J = 7.6 Hz), 7.32–7.35 (m, 4H, ArH), 7.45–7.47 (m, 5H, ArH and NH), 7.57–7.59 (dd, 2H, ArH, J = 1.6 and 4.8 Hz), 7.68 (s, 1H, N=CH), 7.84–7.87 (dd, 2H, ArH, J = 2.0 and 6.8 Hz), 8.18–8.20 (d, 2H, ArH, J = 7.6 Hz). ¹³C-NMR (CDCl₃, 400 MHz δ (ppm)): 145.4 (C=N), 142.5 (NHC), 140.6 (2C), 137.2, 134.2, 129.4 (2C), 120.4 (2C), 114.5 (2C), 113.8 (2C), 110.0 (2C).



Figure 2. The absorption spectra of D-π-A structured carbazole–formazan dyes (**6A–C**) in (a) chloroform, (b) toluene, and (c) acetonitrile. [Color figure can be viewed at wileyonlinelibrary.com]

General procedure of synthesis of D-A and D-π-A carbazole-formazan derivatives. The carbazole hydrazones 3 and 4 (5 mmol) in N.N-dimethyl formamide (50 mL) were added to pyridine (25 mL), which were used for basic pH. In another flask, benzenediazonium chloride solution was prepared using aniline (5 mmol), concentrated HCl (5 mL), and sodium nitrite (5 mmol) at -5° C. This solution was added to the carbazole hydrazone 3 and/or 4 solution dropwise with constant stirring to form carbazole-based formazans. The final solution was stirred for 2 h at the same temperature, and then 50-mL cold water was added to this mixture, and the solid obtained was filtered [41-43]. All the other formazans were synthesized by the same way. All the compounds synthesized were chromatographed with ethyl acetate-hexane (1:5) solvent mixture using silica gel for purification. Organic solvents were evaporated to obtain D-A carbazole-formazan derivatives such as 3-(9-methyl9*H*-carbazol-3-yl)-1,5-diphenylformazan (**5**A), 5-(4methylphenyl)-3-(9-methyl-9*H*-carbazol-3-yl)-1-phenylfor mazan (**5**B), 5-(4-nitrophenyl)-3-(9-methyl-9*H*-carbazol-3yl)-1-phenylformazan (**5**C), and D- π -A carbazole– formazan derivatives such as 3-(4-(9*H*-carbazol-9-yl) phenyl)-1,5-diphenylformazan (**6**A), 5-(4-methylphenyl)-3-(4-(9*H*-carbazol-9-yl)phenyl)-1-phenylformazan (**6**B), and 5-(4-nitrophenyl)-3-(4-(9*H*-carbazol-9-yl)phenyl)-1phenylformazan (**6**C).

3-(9-Methyl-9*H***-carbazol-3-yl)-1,5-diphenylformazan** (5A). Cherry-red solid; yield: 0.40 g (50%); mp: 195°C; IR (KBr, cm⁻¹) v: 3423 (NH), 1595 (C=N), 1492 (N=N), 1322 (C–N). ¹H-NMR (CDCl₃, 400 MHz, δ (ppm)): 3.75 (s, 3H, –NCH₃), 7.16–7.22 (m, 4H, ArH), 7.30–7.34 (t, 2H, ArH, J = 8.0 Hz), 7.30–7.42 (m, 5H, ArH), 7.62– 7.64 (d, 4H, ArH, J = 8.4 Hz,), 8.10–8.12 (d, 1H, ArH, J = 8.0 Hz), 8.18–8.20 (d, 1H, ArH, J = 8.8 Hz), 8.73 (s, 1H, NH). ¹³C-NMR (CDCl₃, 400 MHz, δ (ppm)): 155.0 Month 2019

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Figure 3. Emission and excitation spectra of D-A structured carbazole–formazan dyes (5A–C) in (a) chloroform, (b) toluene, and (c) acetonitrile. [Color figure can be viewed at wileyonlinelibrary.com]

5-(4-Methylphenyl)-3-(9-methyl-9*H*-carbazol-3-yl)-1phenylformazan (5B). Dark pink-red solid; yield: 0.23 g

phenylformazan (5B). Dark pink-red solid; yield: 0.23 g (32%); mp: 142°C; IR (KBr, cm⁻¹) v: 3425 (NH), 1595 (C=N), 1494 (N=N), 1325 (C-N). ¹H-NMR (CDCl₃, 400 MHz, δ (ppm)): 2.46 (s, 3H, CH₃), 3.87 (s, 3H, NCH₃), 7.18–7.21 (t, 1H, ArH, J = 7.6 Hz), 7.26–7.34 (m, 4H, ArH), 7.41–7.53 (m, 5H, ArH), 7.61–7.63 (d, 2H, ArH, J = 7.6 Hz), 8.21–8.23 (d, 1H, ArH, J = 7.6 Hz), 8.28–8.31 (dd, 1H, ArH, J = 6.8 and 1.6 Hz), 8.84 (s, 1H, NH). ¹³C-NMR (CDCl₃, 400 MHz, δ (ppm)): 155.0

5-(4-Nitrophenyl)-3-(9-methyl-9H-carbazol-3-yl)-1-

phenylformazan (5C). Dark red solid; yield: 0.56 g (75%); mp: 186°C; IR (KBr, cm⁻¹) v: 3422 (NH), 1590 (C=N), 1590–1368 (NO₂), 1518 (N=N), 1324 (C–N). ¹H-NMR (CDCl₃, 400 MHz, δ (ppm)): 3.77 (s, 3H, NCH₃), 7.23–7.38 (m, 6H, ArH), 7.46–7.55 (m, 4H, ArH), 7.82–7.87 (m, 2H, ArH), 8.04–8.23 (m, 4H, ArH), 8.68 (s, 1H, NH). ¹³C-NMR (CDCl₃, 400 MHz, δ (ppm)): 155.4 (C=N), 150.5 (N=N-C), 145.5 (NHC), 143.3, 142.5, 141.9, 129.4 (2C), 127.7, 126.8, 126.4,



Figure 4. Emission and excitation spectra of D- π -A structured carbazole–formazan dyes (6A–C) in (a) chloroform, (b) toluene, and (c) acetonitrile. [Color figure can be viewed at wileyonlinelibrary.com]

126.2, 124.7, 124.6 (2C), 123.4, 123.2, 122.3 (2C), 120.7, 120.5, 114.5 (2C), 109.6, 109.4, 29.4 (NCH₃). HRMS (ESI +): analytically calculated for $(C_{26}H_{20}N_6O_2)$ 449.1726, found 449.1771.

3-(4-(9*H***-Carbazol-9-yl)phenyl)-1,5-diphenylformazan** (6A). Red-brown solid; yield: 0.52 g (80%); mp: 212°C. IR (KBr, cm⁻¹) v: 3422 (NH), 1598 (C=N), 1450 (N=N), 1226 (C-N). ¹H-NMR (CDCl₃, 400 MHz, δ (ppm)): 7.31–7.35 (m, 4H, ArH), 7.43–7.54 (m, 8H, ArH and NH), 7.65–7.67 (d, 2H, ArH, J = 8.4 Hz), 7.75–7.77 (dd, 4H, ArH, J = 1.2 and 7.2 Hz), 8.18–8.20 (d, 2H, ArH, J = 8.0 Hz), 8.37–8.40 (dd, 2H, ArH, J = 1.6 and 5.2 Hz), 15.52(s, 1H, NH). ¹³C-NMR (CDCl₃, 400 MHz, δ (ppm)): 153.1 (C=N), 147.8 (N=N-C and NHC), 140.8 (2C), 136.9, 136.6, 129.5 (4C), 127.7 (2C), 127.2 (2C), 126.9 (2C), 126.0 (2C), 123.4 (2C), 120.3 (2C), 119.9 (2C), 118.9 (4C), 109.9 (2C). HRMS (ESI+): analytically calculated for $(C_{31}H_{23}N_5)$ 466.2032, found 466.2032.

5-(4-Methylphenyl)-3-(4-(9*H***-carbazol-9-yl)phenyl)-1phenylformazan (6B).** Dark purplish red solid; yield: 0.44 g (66%); mp: 225°C. IR (KBr, cm⁻¹) v: 3422 (NH), 1598 (C=N), 1450 (N=N), 1233 (C–N). ¹H-NMR (CDCl₃, 400 MHz, δ (ppm)): 2.46 (s, 3H, CH₃), 7.22–7.24 (m, 2H, ArH), 7.31–7.35 (m, 4H, ArH), 7.44–7.49 (m, 4H, ArH), 7.53–7.55 (d, 2H, ArH, *J* = 8.0 Hz), 7.64–7.67 (m, 3H, ArH), 7.75–7.77 (d, 2H, ArH, *J* = 8.0 Hz), 8.18–8.20 (d, 2H, ArH, *J* = 8.0 Hz), 8.38–8.40 (d, 2H, ArH, *J* = 8.0 Hz), 15.23 (s, 1H, NH). ¹³C-NMR (CDCl₃, 400 MHz, δ (ppm)): 155.2 (C=N), 150.5 (N=N-C), 145.4 (NHC), 140.3 (2C), 137.2, 132.4, 131.8, 129.3 (2C), 128.9 (2C), 127.0 (2C), 126.2 (2C), 124.7, 123.6 (2C), 122.3 (2C), 120.8 (2C), 120.4 (2C), 114.5 (2C), 113.9 (2C), 110.0 (2C), 21.3 (ArCH₃). HRMS (ESI+): analytically calculated for (C₃₂H₂₅N₅) 480.2188, found 480.2188.

5-(4-Nitrophenyl)-3-(4-(9H-carbazol-9-yl)phenyl)-1-

phenylformazan (6C). Red-dark purple solid; yield: 0.60 g (85%); mp: 198°C. IR (KBr, cm⁻¹) v: 3426 (NH), 1596 (C=N), 1449 (N=N), 1226 (C-N). ¹H-NMR (CDCl₃, 400 MHz, δ (ppm)): 7.30–7.32 (m, 3H, ArH), 7.43-7.45 (m, 2H, ArH), 7.52-7.54 (d, 4H, ArH, J = 8.8 Hz), 7.60–7.62 (m, 2H, ArH), 7.69–7.71 (d, 2H, ArH, J = 8.4 Hz), 7.80–8.02 (m, 2H, ArH), 8.16–8.18 (d, 2H, ArH, J = 8.0 Hz), 8.28-8.31 (d, 2H, ArH, J = 8.4 Hz), 8.36–8.38 (d, 2H, ArH, J = 8.4 Hz), 15.52 (s, 1H, NH). ¹³C-NMR (CDCl₃, 400 MHz, δ (ppm)): 156.0 (C=N), 150.5 (N=N-C), 145.8 (NHC), 140.6 (2C), 140.5, 137.2, 131.7, 130.0 (2C), 126.5 (2C), 126.2 (2C), 125.2 (2C), 124.8, 123.6 (2C), 121.0 (2C), 121.0 (2C), 117.4 (2C), 114.9 (2C), 113.9 (2C), 109.8 (2C). HRMS (ESI+): analytically calculated for $(C_{31}H_{22}N_6O_2)$ 511.1882, found 511.1903.

CONCLUSION

With this study, first, carbazole-based new carbazoleformazan compounds with D-A/D- π -A structures were according to the literature. For this aim, carbazoleformazan dyes were synthesized and characterized, and then their spectrophotometric and spectrofluorimetric properties were studied for 1×10^{-5} M in the different polarity solvents. According to Stokes's shift calculation of the compounds, D- π -A structured carbazole–formazan dye **6C** was shown the highest value owing to presence of electron acceptor nitro group at the para position and the π -conjugated bridge.

Considering the photophysical results of the newly synthesized carbazole–formazan dyes, D- π -A structured derivatives are expected to be used in dye industry that develops every day.

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