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Clean and Efficient Green Protocol of *N,N′*-Bis(2-(arylazo)-2-(aroyl)vinyl)ethane-1,2-diamines in Aqueous Medium without Catalyst: Synthesis and Photophysical Characterization

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R/Ar = 2-thienyl; 2(4)-XC$_6$H$_4$: X = H. NO$_2$, Cl, Br, F, MeO, Me
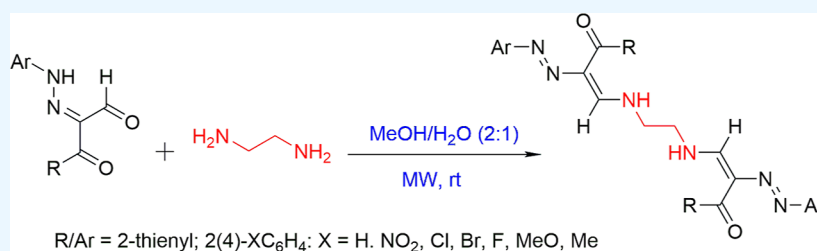
ABSTRACT: An interesting platform for the construction of novel *N,N′*-bis(2-(arylazo)-2-(aroyl)vinyl)ethane-1,2-diamines is reported in this work. These bis-arylazo compounds were assembled based on the reaction of ethylenediamine with various 2-arylhydrazono-3-oxopropanals in aqueous conditions under both conventional stirring and microwave conditions at ambient temperature. The factors affecting the optimization conditions were intensively practiced. The structures of the new products were established from their spectroscopic analyses and X-ray single crystals. The photophysical behavior of the bis-arylazo derivatives was examined. The UV−vis spectra showed maximum absorption band in the range of 348−383 nm with molar extinction coefficients ranging from 0.89×10^4 to 4.02×10^4 M^{-1} cm^{-1}. The highest molar absorptivity coefficient ($\sim 45 \times 10^3$ M^{-1} cm^{-1}) was observed in CHCl$_3$ solvent. The fluorescence properties showed that some compounds were interesting fluorophore materials with high Stokes shifts. The photoluminescence study of some compounds was promising, with maximal emission peaks ranging between 417−436 nm.

1. INTRODUCTION

Substituted amines are important pharmacophores in a wide range of biologically active compounds. Several amine derivatives are presented to have potent analgesic, antiparasitic, antifungal, and antibacterial activities.[1,2] They also behaved as promising electronic materials with semiconductive and piezoelectric properties.[3−5] Bis-amines are good substrates for the synthesis of carbon fiber reinforced composite materials,[6] with highly promising biological applications, such as antimicrobial[7,8] and anticancer[9−14] activities. On the other side, bis-enaminones are versatile multifunctional substrates with wide applications in combinatorial chemistry and are employed as precursors in synthesizing several heterocyclic systems.[15−17] They are also involved as ligands in the synthesis of liquid crystalline metallocomplexes and polymer materials.[18,19]

The reaction of 1,3-dicarbonyl compounds with diaminoalkanes can produce various products based on the reaction conditions. For example, the reaction of 1,3-diketones and diamines can either result in *N,N′*-ethylene-bis(1,3-aminovinyl ketones)[20,21] or 1,4-diazepine derivatives.[22−24] In the presence of nickel(II), 1,3-diketones and ethylenediamine reacted together to yield the nickel chelates of *N,N′*-bis(2-(arylazo)-2-(aroyl)vinyl)ethane-1,2-diamines.[25,26]

Direct condensation of amines with dicarbonyl compounds at reflux under azeotropic water removal conditions resulted in the formation of enaminoketones.[27] This reaction was conducted using a number of catalysts such as Zn(ClO$_4$)$_2$·6H$_2$O,[28] β-cyclodextrin in water,[29] metal salts,[30−33] VO-(acac)$_2$,[34] metal triflates,[35−38] metal oxides,[39,40] Bi(TFA)$_3$,[33] solid supported reagents,[41−44] ceric ammonium nitrate,[45] trimethylsilyl trifluoromethanesulfonate (TMSTf),[46] [(PPh$_3$)-AuCl]/AgOTf,[47] formic acid,[48] ionic liquids,[49] tris-(hydrogensulfato)boron or trichloroacetic acid,[50] K-10/ultrasound,[51] microwave (MW)-assisted,[52,53] and phosphomolybdic acid (PMA).[54] However, some of such approaches have synthetic drawbacks, such as longer reaction times, use of toxic solvents, low yields, use of excess amounts of catalyst, use of

toxic metal catalysts, lack of selectivity, and, in some cases, catalyst preparation requires tedious workup procedures.

Therefore, the current study aims to find alternative conditions for the synthesis of N,N′-bis(2-(arylazo)-2-(aroyl)-vinyl)ethane-1,2-diamines with the achievement of the following goals: (1) milder reaction conditions, (2) high product yield, (3) shorter reaction time, and (4) encourage cost-effective and green experimental procedures. These goals were accomplished by carrying out the reaction under MW and environmentally favorable water solvent, where water is the most proper solvent for a green environment.[55−57] In addition, utilizing MW energy speeds up organic reactions, resulting in cleaner products, higher yields, and better time management.[58−66] In continuation of our research projects involving various green conditions (water, ultrasonic, MW irradiation, and metal catalysts) for the functionalization of several ketohydrazonals and various reactive substrates,[67−74] we herein carry out a green synthetic protocol for the construction of various N,N′-bis(2-(arylazo)-2-(aroyl)vinyl)ethane-1,2-dia-mines via reaction of 3-ketohydrazonals with ethylenediamine under aqueous conditions.

2. RESULTS AND DISCUSSION

2.1. Chemistry. The highly reactive substrates: 2-arylhydrazono-3-oxopropanals **1a–o** were assembled following the previously reported procedures in the literature.[75,76] Afterward, a demonstrative reaction example was carried out by treating ethylenediamine **2** with two equivalents of 2-(4-chlorophenyl)hydrazono-3-oxopropanal **1a**. The variation of reaction solvents and heating modes on the reaction productivity was thoroughly examined (Table 1 and Scheme 1). The reaction was followed by thin-layer chromatography (TLC). Conducting the reaction in solvents such as DMF,

Table 1. Optimization of the Condensation Reaction Condition of 1a with 2[a]

entry	solvent	temp. °C	conventional (90 min) yield (%)	MW (15 min) yield (%)
1	DMF	rt	16	25
2	acetic	rt	18	28
3	toluene	rt	25	36
4	cyclohexane	rt	22	32
5	chloroform	rt	28	37
6	1,4 dioxane	rt	35	45
7	H$_2$O	rt	66	76
8	propanol	rt	50	61
9	isobutanol	rt	64	75
10	ethanol	rt	60	70
11	methanol	rt	69	80
12	**methanol/H$_2$O (2:1)**	**rt**	**80**	**92**
13	methanol/H$_2$O (2:1)	100	65	75
14	methanol/H$_2$O (2:1)	50	68	79
15	methanol/H$_2$O (1:1)	rt	74	85
16	methanol/H$_2$O (1:2)	rt	72	83

[a]Reaction conditions: **1a** (1 mmol), **2** (0.5 mmol), and solvent (9 mL); stirrer for 90 min at rt, for 15 min MW irradiation (200 W) at 25 °C.

acetic acid, toluene, cyclohexane, chloroform, or 1,4-dioxane at room temperature (rt) for 90 min (entries 1–6, Table 1), afforded low yields of the bis-arylazo derivative **3a** of 12 to 35%. When the same reaction conditions were performed under MW irradiation, the isolated yields increased to 25 to 45%. Later, when the reaction was conducted in water, the isolated product yield increased to 66 and 76% under thermal and MW conditions at rt, respectively (entry 7, Table 1). Repeating the same reaction using propanol, isobutanol, ethanol, or methanol solvents resulted in the formation of compound **3a** in 50−69% under thermal condition at rt, compared with 61−80% yields under MW (entries 8−11, Table 1). However, methanol/H$_2$O mixed solvent (2:1) was found to be the optimal reaction solvent in both thermal and MW conditions at rt, where the formation of **3a** was accomplished in 80 and 92% yield, respectively (entry 12, Table 1). It was reported that polar solvents facilitate reactions to proceed faster under MW conditions where they absorb MW energy faster than thermal mode. When the same reaction was repeated at 100 °C, the isolated product of **3a** decreased to 65 and 75% under thermal and MW conditions, respectively (entry 13, Table 1). Also, when further lowering the temperature to 50 °C, compound **3a** yielded 68 and 79% under thermal and MW conditions, respectively (entry 14, Table 1). Changing the ratio of methanol/water to (1:1) led to the formation of the bis-arylazo derivative **3a** to 74 and 85% yields under thermal and MW conditions, respectively (entry 15, Table 1). Finally, repeating the same reaction conditions using a methanol/water (1:2) aqueous solvent dropped the yield of compound **3a** to 72 and 83% under thermal and MW conditions, respectively (entry 16, Table 1). The structure of product **3a** was established from its elemental and spectroscopic analyses (IR, ¹H- and ¹³C NMR, MS, and HRMS).

From the above results, decreasing the yield with an increasing temperature can be attributed to both thermodynamic and kinetic factors influencing the reaction. At elevated temperatures, reactants or intermediates involved in the condensation reaction may undergo decomposition or give undesired side products, leading to a decrease in the product yields. Such thermal degradation is common in reactions involving sensitive organic compounds, where optimal yields are often achieved at lower temperatures. This agrees with the observed significant drop in the yield of compound **3a** at 100 °C compared to rt, suggesting that higher temperatures promote undesired reactions or decompose intermediates, thereby reducing the efficiency of the desired products.
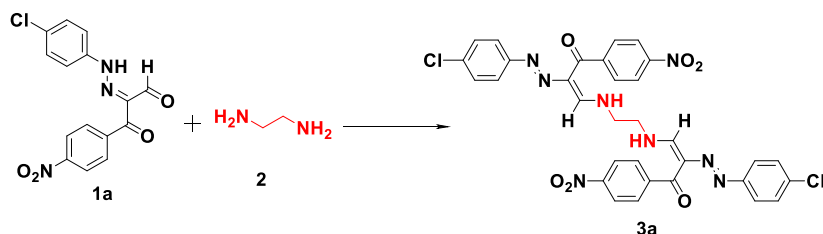
The optimal reaction conditions obtained from Table 1 were utilized to construct a library of the bis-arylazo derivatives **3a–o** (Table 2). Thus, treatment of various 2-(aryl)hydrazono-3-oxopropanal **1a–o** with ethylenediamine **2** in a 2:1 molar ratio in methanol/H$_2$O mixed solvent (2:1 v/v) was carried out at rt under both conventional stirring and MW irradiating conditions (Scheme 2). Conducting the reaction under MW conditions resulted in an increase in the production yields of compounds **3a–o** compared to conventional stirring. The conventional condition yields varied between 50 and 80%, but the yields increased under MW conditions to be ranged between 59 to 92%. Studying the effect of variation of the electronic behaviors of the 2-(aryl)hydrazono-3-oxopropanal **1a–o** substrates was also achieved. It was found that substrate **1** having highly electron-withdrawing substituents such as NO$_2$ and Cl (where Ar = 4-ClC$_6$H$_4$ and R = 4-NO$_2$C$_6$H$_4$) provided the highest yield under both conventional stirring and MW

Scheme 1. Reaction of the Arylhydrazonopropanal 1a with Ethylenediamine 2

Table 2. Synthesis of the Bis(arylazo) Derivatives 3a−o under Conventional and MW Conditions[a]

entry	products	R	Ar	conv. (90 min) yields[b]	MW (10 min) yields[b]
1	3a	4-NO$_2$C$_6$H$_4$	4-ClC$_6$H$_4$	80	92
2	3b	4-NO$_2$C$_6$H$_4$	4-BrC$_6$H$_4$	75	88
3	3c	4-NO$_2$C$_6$H$_4$	C$_6$H$_5$	68	75
4	3d	4-ClC$_6$H$_4$	C$_6$H$_5$	70	82
5	3e	4-ClC$_6$H$_4$	4-BrC$_6$H$_4$	72	80
6	3f	4-BrC$_6$H$_4$	4-ClC$_6$H$_4$	62	73
7	3g	4-FC$_6$H$_4$	4-ClC$_6$H$_4$	74	85
8	3h	4-FC$_6$H$_4$	4-BrC$_6$H$_4$	72	82
9	3i	4-OMeC$_6$H$_4$	4-BrC$_6$H$_4$	53	63
10	3j	4-OMeC$_6$H$_4$	4-ClC$_6$H$_4$	54	63
11	3k	C$_6$H$_5$	4-ClC$_6$H$_4$	57	66
12	3l	C$_6$H$_5$	4-BrC$_6$H$_4$	55	66
13	3m	C$_6$H$_5$	o-NO$_2$C$_6$H$_4$	50	59
14	3n	2-thienyl	4-CH$_3$C$_6$H$_4$	67	76
15	3o	2-thienyl	C$_6$H$_5$	69	78

[a]Reaction condition: **1a−o** (1 mmol) and ethylenediamine (**2**) (0.5 mmol), in MeOH/H$_2$O (2:1) (9 mL), stirrer at rt for 90 min, MW irradiation (200 W) at 25 °C for 15 min. [b]Isolated yields.

irradiation conditions. The lowest yields were obtained for substrates **1** having electron-releasing substituents, such as methyl or methoxy groups. All structures of the obtained pure products were fully characterized using spectral analyses as well as X-ray single crystals of a demonstrative compound **3k** (Figure 1).[77] A suggested reaction mechanism for the formation of a demonstrative example of the bis-arylazo derivatives **3a−o** is described in Scheme 3.

2.2. Photophysical Studies. The photophysical behavior of the bis-diamine derivatives **3a−o** presented in Table 3, showing the variation of electronic behavior of the substituents, has been studied. As shown in Figure 2a, the UV−vis spectrum of the dichloromethane solution of **3a−o** showed the maximum absorption band (λ_{max}) in the range of 348−383 nm. This can be attributed to $n \rightarrow \pi^*$ and/or $\pi \rightarrow \pi^*$ electronic transitions of azo chromophores with molar extinction coefficients ranging from 0.89×10^4 to 4.02×10^4
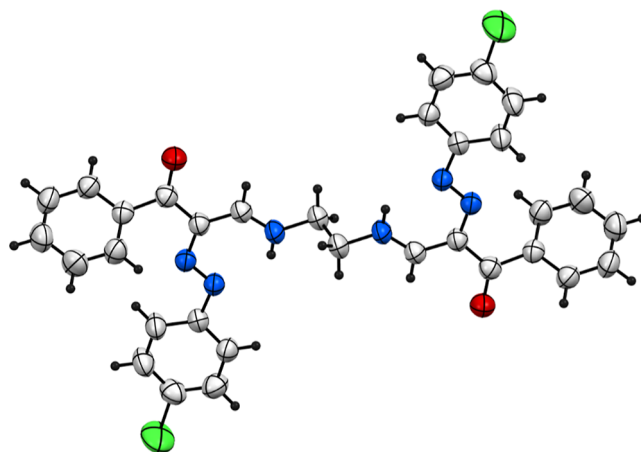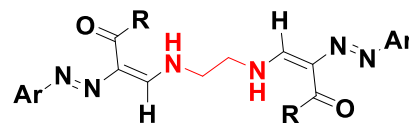

**Figure 1.** X-ray single crystals of compound **3k** obtained from diffraction data.

M^{-1} cm^{-1}. Meanwhile, the measured molar extinction coefficient ($\varepsilon_{max/abs}$) for **3h** is $\sim 3.69 \times 10^4$ M^{-1} cm^{-1} at 378 nm, which appeared to be higher than the corresponding values for **3b** ($\varepsilon_{max/abs} \sim 1.28 \times 10^4$ M^{-1} cm^{-1} at 375 nm) and **3i** ($\varepsilon_{max/abs} \sim 3.01 \times 10^4$ M^{-1} cm^{-1} at 383 nm) (Table 4).


The UV−vis absorption spectra of all of the prepared bis-arylazo derivatives are shown in Figure 2a. The derivatives that have varied substitutions R at the 1-prop-2-enone moiety (**3b**, **3e**, **3h**, **3i**, and **3l**) have band range 353−383 nm (Table 4), **3i** (383 nm) > **3h** (378 nm) > **3b**, **3e** (375 nm) > **3l** (353 nm). When the electron-donating substituent (methoxy group) was introduced at the phenyl group of the 1-prop-2-enone (**3i**), the absorption spectra gave a considerable redshift (383 nm).

The fluorescence properties of **3a−o** in DMSO were also studied (Figure 2b). We found that the emission maximum emerges in the visible region, which appeared in the 389−441 nm range. This may be attributed to the azo forms of the synthesized bis-arylazo derivatives (Table 4). It was found that the emission maximum wavelength was little affected by the

Scheme 2. Reaction of Arylhydrazonopropanals 1a−o with Ethylenediamine 2
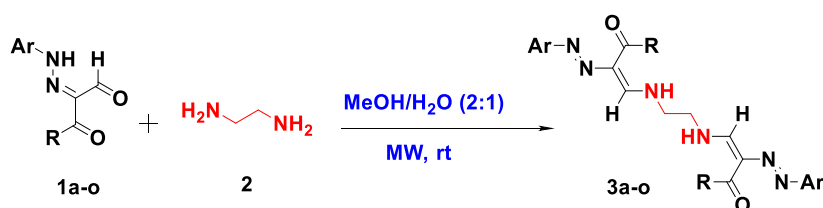
Scheme 3. Proposed Reaction Mechanism for the Formation of 3a
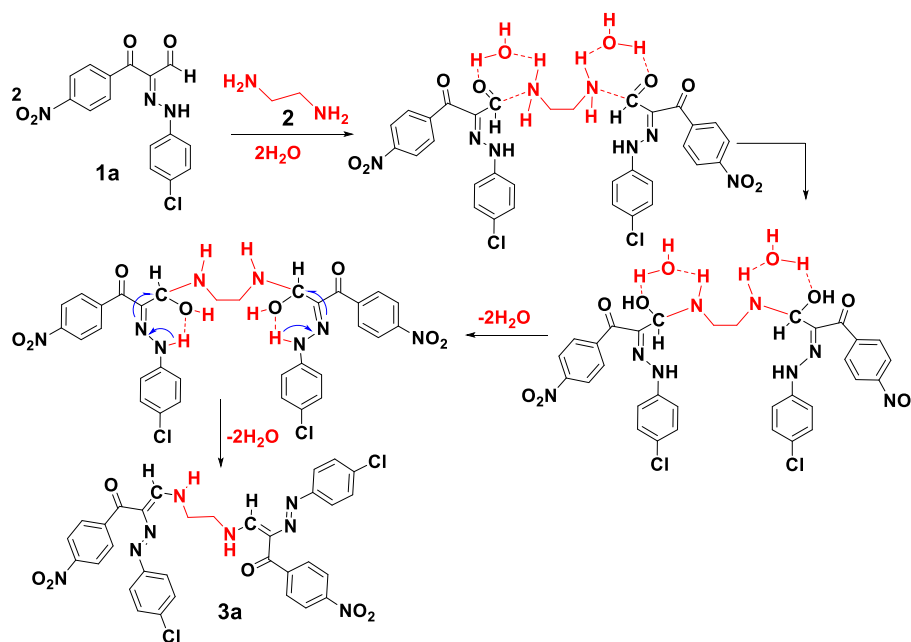
Table 3. Molecular Structures of the Bis-Arylazo Derivatives 3a–o

entry	bis-arylazo compds	R	Ar
1	**3a**	$4\text{-}NO_2C_6H_4$	$4\text{-}ClC_6H_4$
2	**3b**	$4\text{-}NO_2C_6H_4$	$4\text{-}BrC_6H_4$
3	**3c**	$4\text{-}NO_2C_6H_4$	C_6H_5
4	**3d**	$4\text{-}ClC_6H_4$	C_6H_5
5	**3e**	$4\text{-}ClC_6H_4$	$4\text{-}BrC_6H_4$
6	**3f**	$4\text{-}BrC_6H_4$	$4\text{-}ClC_6H_4$
7	**3g**	$4\text{-}FC_6H_4$	$4\text{-}ClC_6H_4$
8	**3h**	$4\text{-}FC_6H_4$	$4\text{-}BrC_6H_4$
9	**3i**	$4\text{-}OMeC_6H_4$	$4\text{-}BrC_6H_4$
10	**3j**	$4\text{-}OMeC_6H_4$	$4\text{-}ClC_6H_4$
11	**3k**	C_6H_5	$4\text{-}ClC_6H_4$
12	**3l**	C_6H_5	$4\text{-}BrC_6H_4$
13	**3m**	C_6H_5	$o\text{-}NO_2C_6H_4$
14	**3n**	2-thienyl	$4\text{-}CH_3C_6H_4$
15	**3o**	2-thienyl	C_6H_5

nature of the substituent R in the derivatives **3a–e**. Bathochromic shift was evoked more effectively by the electron-withdrawing substituents than by the electron-donating substituents. The highest bathochromic shift was observed for the derivative **3i** with a methoxy substituent.

The Stokes shifts of the bis-arylazo compounds **3a–o** were evaluated and found to range between 41 and 81 nm (Table 4), indicating promising fluorescence characteristics that make them suitable candidates for photonic device applications. Notably, compound **3l**, featuring a bromo substituent on the phenyl ring of the 1-prop-2-enone moiety, exhibited the largest Stokes shift of 81 nm and demonstrated an absorption maximum at 353 nm. In contrast, compound **3m**, bearing a nitro group at the ortho position of the aryl ring, displayed the smallest Stokes shift of 41 nm with an absorption peak at 349 nm.

The absorption properties of compound **3g** were measured in eight solvents; methanol (protic solvent), ethyl acetate (EtOAc), tetrahydrofuran (THF), chloroform, toluene,

acetone, acetonitrile, and dimethyl sulfoxide (DMSO) (polar aprotic solvents), as presented in Figure 3. The UV−vis absorption maxima and extinction coefficients are given in Table 5. The absorption spectra of compound **3** (Figure 3) showed maximum absorption in the range of 370−385 nm. This could be related to the azo group and demonstrate apparent solvatochromic performance. Generally, the absorption maximum of **3g** was slightly blue-shifted when dissolved in more polar solvents, for example, $CHCl_3$ (385 nm) > THF (379 nm) > acetone (376 nm) > DMSO (375 nm). However, a slight blue shift of 15 nm was observed for the protic solvent MeOH.

Additionally, the highest molar absorptivity coefficients ($\sim 45 \times 10^3$ M^{-1} cm^{-1}) were found in $CHCl_3$, acetone, and toluene; however, the median absorptivity coefficients ($\sim 42 \times 10^3$ M^{-1} cm^{-1}) were observed in acetonitrile and EtOAc. The lowest absorptivity coefficient ($\sim 32 \times 10^3$ M^{-1} cm^{-1}) was noted in DMSO, methanol, and THF (Table 5).

The photoluminescence (PL) study of compound **3g** in different solvents is shown in Figure 4. Herein, it was observed that the solvent effect was more pronounced in the maximal emission peak range between 417 and 436 nm: for example, toluene (434 nm), $CHCl_3$ (436 nm), THF (429 nm), EtOAc (425 nm), and acetone (424 nm) (Table 5). However, in the polar aprotic solvents: CH_3CN (422 nm) and DMSO (424 nm) and, in the polar protic solvent, MeOH (417 nm). Compound **3g** displayed an increasing blue shift as the polarity of the solvent increased. This could be caused by many reasons, one of which is (1) change in the nature of the emitting state induced by the solvent; (2) dipole−dipole interactions between solute and the solvent; and (3) specific solute−solvent interactions, such as H-bonding.

Thus, the spectroscopic data indicated a correlation between the nature of the substituents on the bis-arylazo derivatives and their photophysical properties. Specifically, a systematic trend was observed, where electron-withdrawing groups, such as (NO_2) and (Cl), consistently resulted in a red shift in both absorption and emission wavelengths. This red shift was
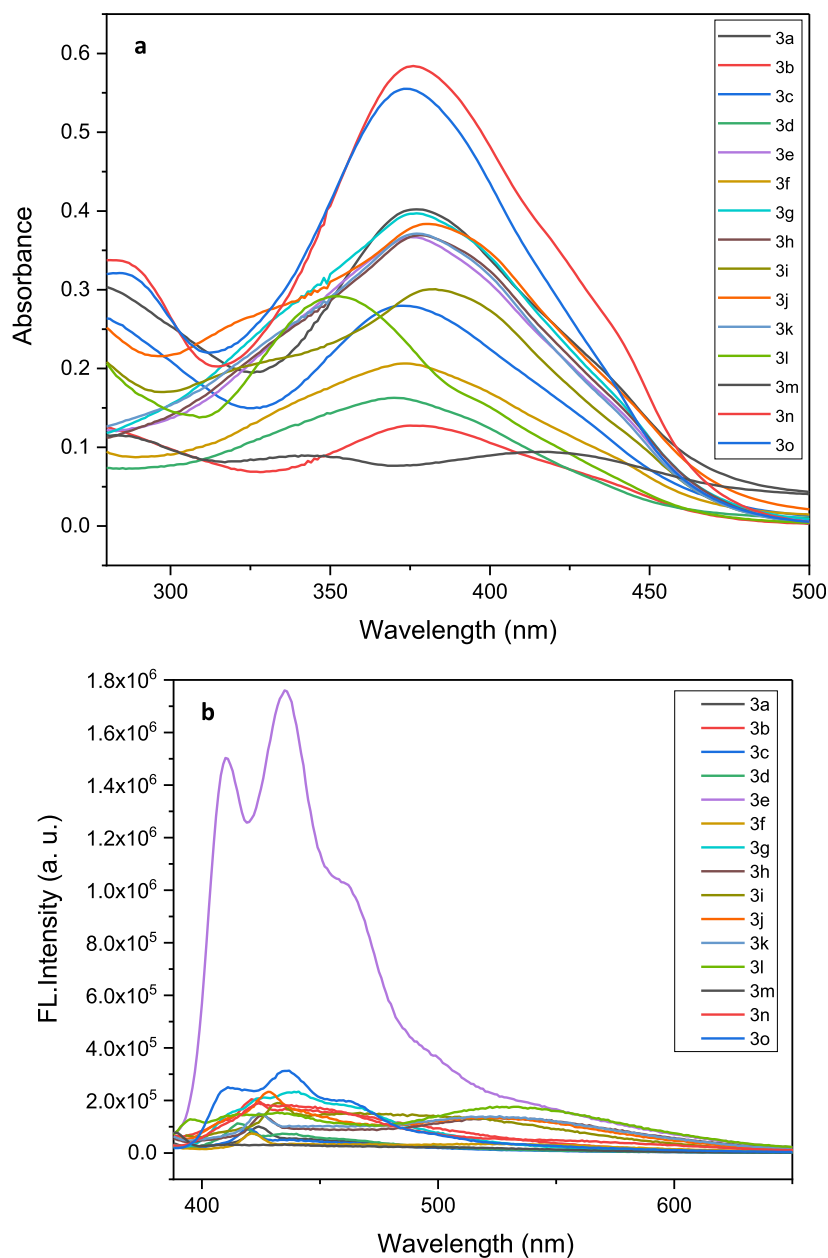
Figure 2. (a) UV−vis spectra of the bis-arylazo derivatives **3a−o** recorded in DMSO. (b) Emission spectra of the bis-arylazo derivatives **3a−o** recorded in DMSO.

attributed to the reduction in the energy gap between the excited and ground states. For example, compound **3a** (4-$NO_2C_6H_4$/4-ClC_6H_4) exhibited absorption and emission maxima at 377 and 424 nm, respectively, while compound **3b** (4-$NO_2C_6H_4$/4-BrC_6H_4) showed absorption at 375 nm and emission at 421 nm.

Conversely, electron-donating groups like methoxy (OCH_3) and methyl (CH_3) induce a blueshift, reflecting a higher energy transition due to an increased energy gap. For instance, compound **3i** (4-$OMeC_6H_4$/4-BrC_6H_4) displayed an absorption maximum at 383 nm and an emission maximum at 432 nm, while compound **3n** (4-$CH_3C_6H_4$/2-thienyl) had absorption and emission maxima at 376 and 424 nm, respectively.

In summary, the substituents' electronic properties significantly affected the absorption and emission spectra, with electron-withdrawing groups causing red shifts and electron-

donating groups leading to blue shifts. These systematic trends provide a clear understanding of how substituent variations influence the photophysical behavior of the synthesized compounds.

3. EXPERIMENTAL SECTION

3.1. Materials and Methods. All fine chemicals were highly pure and were purchased from Sigma-Aldrich. The Griffin apparatus was used for measuring the melting points, and they were uncorrected. TLC was established using Polygram SIL G/UV 254 TLC plates, and visualization was performed under UV light at 254 and 365 nm. IR spectra were conducted using KBr disks in a PerkinElmer System 2000 FTIR spectrophotometer. ^{1}H- and ^{13}C NMR spectra were recorded at 600 and 150 MHz, respectively, on a Bruker DPX 400 or 600 superconducting NMR spectrometer, at ambient

Table 4. Photophysical Properties of the Synthesized Bis-Arylazo Derivatives 3a–o

bis-arylazo compds.	absorption[a] $\lambda_{max/abs}$ (nm)	$\varepsilon_{max/abs}$ M^{-1} cm^{-1}	emission[b] $\lambda_{max/em}$ (nm)	Stokes shifts[c] (nm)
3a	377	40,212	424	47
3b	375	12,744	421	46
3c	373	27,971	420	47
3d	370	16,276	415	45
3e	375	36,684	435	60
3f	381	20,073	422	41
3g	376	40,485	441	65
3h	378	36,928	426	48
3i	383	30,076	432	49
3j	380	38,358	429	49
3k	377	37,128	424	47
3l	353	29,172	434	81
3m	348	8955	389	41
3n	376	58,403	424	48
3o	373	55,504	437	64

[a]Determined in DMSO at rt when the concentration of each compound is 1.0×10^{-5} M. [b]Excited at the longest wavelength of the absorption maxima. [c]Stokes shifts are provided as wavelength differences, $\Delta\lambda_{max} = \lambda_{max(em)} - \lambda_{max(ex)}$.
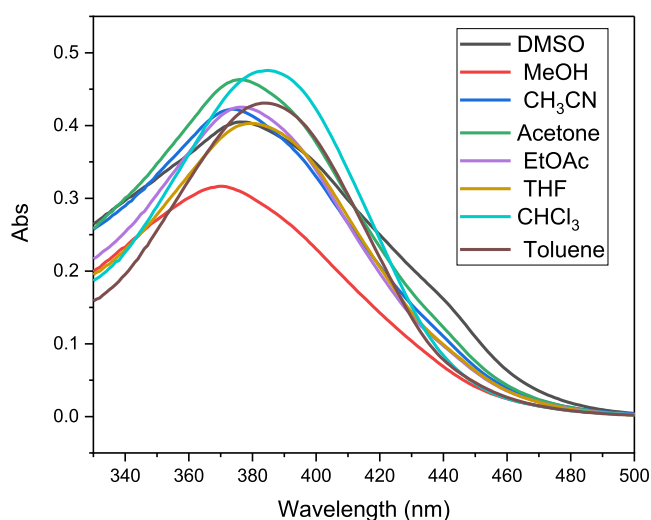
Figure 3. Absorption spectra of the bis-arylazo derivative **3g** in different organic solvents (DMSO, MeOH, CH_3CN, acetone, EtOAc, THF, $CHCl_3$, and toluene).

Table 5. UV–Vis Absorption and Emission Spectra of Compound 3g in Solvents of Varied Polarity[a]

solvent	absorption $\lambda_{max/abs}$	$\varepsilon_{max/abs}$ M^{-1} cm^{-1}	emission[b] $\lambda_{max/em}$
DMSO	375	40,485	424
MeOH	370	31,657	417
CH_3CN	374	42,244	422
acetone	376	46,316	424
EtOAc	377	42,524	425
THF	379	40,287	429
$CHCl_3$	385	47,574	436
toluene	384	43,080	434

[a]Concentration of **3g** 1.0×10^{-5} M in different solvents. [b]Excitations were executed at or near the wavelength position of absorption maxima.

temperature using DMSO-d_6 as a deuterated solvent and TMS as the internal standard (with chemical shifts given in parts per million (ppm)). Low-resolution electron impact mass spectrometry [MS (EI)] and high-resolution [MS (EI)] [HRMS (EI)] were carried out using a high-resolution thermos spectrometer [GC–MS (DFS)] and a magnetic sector mass analyzer at 70.1 eV. MW experiments were conducted using a Discover LabMate CEM MV instrument (300 W with CHEMDRIVER software; Matthews, NC). MW irradiation reactions were carried out in equipped closed-pressured Pyrex tubes. The X-ray single-crystal data were performed, involving a Bruker X8 Prospector and a Rigaku RAXISRAPID diffractometer, and the single-crystal data collection was conducted using Cu Kα radiation at ambient temperature. Solving and refining the structures were performed using the Bruker SHELXTL software package (refinement program-SHELXL97 and structure solution program-SHELXS-97). UV–vis experiments were carried out on a Varian Cary 5 spectrometer from Agilent. Fluorescence assessments were conducted with the Horiba Jobin Yvon-Fluoromax-4 equipped with a time-correlated single-photon counting (TCSPC) module. The 3-oxo-2-arylhydrazonopropanal derivatives **1a–o** were synthesized using the procedures reported in the literature.[53,54]

3.1.1. Synthesis of the N,N′-Bis(2-(arylazo)-2-(aroyl)vinyl)-ethane-1,2-diamine Derivatives 3a–o. 3.1.1.1. General Method A. Ethylenediamine **2** (0.5 mmol) was added dropwise to a solution of the arylhydrazonopropanals **1a–o** (1 mmol) in methanol/H_2O (2:1) (9 mL), and the reaction mixture was mixed thoroughly in a process glass vial. The vial was capped properly and irradiated in a MW synthesis system (200 W) for 15 min at rt, and then volatiles were removed in a vacuum to dryness. The crude product was crystallized from ethanol/DMF to afford the corresponding N,N′-ethylene-bis(arylazo) derivatives **3a–o** as pure products.

3.1.1.2. General Method B. Ethylenediamine **2** (0.5 mmol) was added dropwise to a solution of arylhydrazonopropanals **1a–o** (1 mmol) in methanol/H_2O (2:1) (9 mL). The reaction mixture was stirred for 90 min at rt, and then volatiles were removed in a vacuum to dryness. The crude product was crystallized from ethanol/DMF to afford the corresponding N,N′-ethylene-bis(arylazo) derivatives **3a–o** as pure products.

3.1.1.3. N,N′-Bis(2-((4-chlorophenyl)azo)-2-(4-nitrobenzoyl)vinyl)ethane-1,2-diamine (3a). Yellow crystals, mp 260–261 °C; IR (KBr) ν/cm^{-1}: 3435, 3098, 2930, 1647, 1599, 1540, 1492, 1437, 1277; ^{1}H NMR (DMSO-d_6): δ 3.90 (s, 2H, CH_2), 3.97 (s, 2H, CH_2), 6.81–6.82 (m, 2H, Ar–H, and CH=N), 7.19–7.37 (m, 2H, Ar–H), 7.42–7.45 (m, 2H, Ar–H), 7.46–7.52 (m, 4H, Ar–H), 8.05–8.08 (m, 4H, Ar–H), 8.22–8.30 (m, 4H, CH=N, Ar–H), 12.33 (b, 2H, NH); ^{13}C NMR (DMSO-d_6): δ 60.81, 119.38, 121.96, 122.59, 122.64, 122.99, 123.02, 128.52, 128.84, 128.97, 129.09, 130.11, 130.46, 131.29, 131.63, 131.75, 136.27, 136.41, 141.87, 148.08, 148.43, 149.11, 150.49, 162.29 (Ar–C), 187.99, 189.09 (CO). MS (EI): 685.58 [M]$^+$. HRMS: calcd for $C_{32}H_{24}Cl_2N_8O_6$, 686.1195; found, 686.1190.

3.1.1.4. N,N′-Bis(2-((4-bromophenyl)azo)-2-(4-nitrobenzoyl)vinyl)ethane-1,2-diamine (3b). Yellow crystals, mp 257–258 °C; IR (KBr) ν/cm^{-1}: 3101, 3079, 2924, 1656, 1601, 1540, 1486, 1352, 1299; ^{1}H NMR (DMSO-d_6): δ 3.91 (s, 2H, CH_2), 3.98 (s, 2H, CH_2), 6.83–6.85 (m, 2H, Ar–H, and CH=N), 7.17–7.39 (m, 2H, Ar–H), 7.20–7.32 (m, 2H, Ar–H), 7.46–7.60 (m, 3H, Ar–H), 7.81–7.84 (m, 3H, Ar–
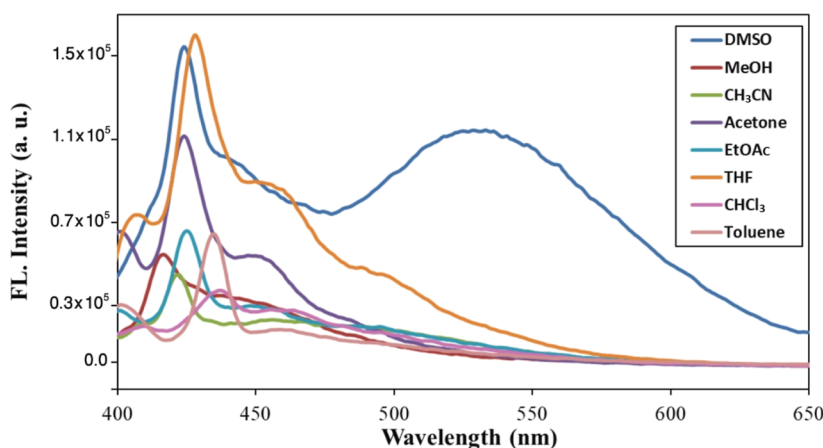
Figure 4. Effect of the solvent polarity of DMSO, MeOH, CH_3CN, acetone, EtOAc, THF, $CHCl_3$, and toluene on the emission spectra of the bis-arylazo compound **3g**.

H), 7.93−8.06 (m, 4H, Ar−H), 8.28−8.29 (m, 2H, CH═N, Ar−H), 12.36 (b, 2H, NH); ^{13}C NMR (DMSO-d_6): δ 60.72, 61.39 (−CH$_2$−), 116.63, 120.17, 122.27, 122.62, 127.97, 131.75, 131.85, 131.96, 131.99, 136.29, 142.25, 142.37, 145.61, 146.04, 148.06, 148.11, 148.20, 148.49, 148.98, 149.10, 162.27 (Ar−C), 187.96, 189.24 (CO). MS (EI): 744.40 [M]$^+$. HRMS: calcd for $C_{32}H_{24}Br_2N_8O_6$, 774.0185; found, 774.0183.

3.1.1.5. N,N′-Bis(2-(phenylazo)-2-(4-nitrobenzoyl)vinyl)-ethane-1,2-diamine (3c). Orange crystals, mp 268−270 °C; IR (KBr) ν/cm$^{−1}$: 3098, 3043, 2940, 1645, 1601, 1586, 1459, 1426, 1278; ^{1}H NMR (DMSO-d_6): δ 3.91 (s, 2H, CH$_2$), 4.00 (s, 2H, CH$_2$), 6.85−6.88 (m, 2H, Ar−H, and CH═N), 7.13−7.26 (m, 4H, Ar−H), 7.49−7.51 (m, 2H, Ar−H), 7.84−7.95 (m,, 4H, Ar−H), 8.07−8.08 (m, 3H, Ar−H), 8.31−8.33 (m, 5H, Ar−H, and CH═N), 12.53 (b, 2H, 2NH); ^{13}C NMR (DMSO-d_6): δ 60.39, 61.27 (−CH$_2$−), 116.45, 119.37, 121.18, 122.12, 122.99, 123.38, 123.57, 128.03, 128.45, 129.36, 129.98, 130.46, 131.29, 136.26, 141.86, 142.40, 144.70, 148.43, 148.60, 151.89, 152.02, 156.30, 156.36 (Ar−C), 185.10, 187.99 (CO). MS (EI): 617.82 [M]$^+$. HRMS: calcd for $C_{32}H_{26}N_8O_6$, 618.1975; found, 618.1974.

3.1.1.6. N,N′-Bis(2-(phenylazo)-2-(4-chlorobenzoyl)vinyl)-ethane-1,2-diamine (3d). Yellow crystals, mp 230−231 °C; IR (KBr) ν/cm$^{−1}$: 3066, 3044, 2929, 1641, 1600, 1540, 1487, 1427, 1277; ^{1}H NMR (DMSO-d_6): δ 3.89 (s, 2H, CH$_2$), 4.00 (s, 2H, CH$_2$), 6.84 (s, 2H, Ar−H, and CH═N), 7.18−7.19 (m, 2H, Ar−H), 7.38−7.58 (m, 4H, Ar−H), 7.79−7.80 (m, 4H, Ar−H), 7.81−7.91 (m, 5H, Ar−H), 8.22−8.28 (m, 3H, CH═N, Ar−H), 12.70 (b, 1H, NH), 12.92 (b, 1H, NH); ^{13}C NMR (DMSO-d_6): δ 61.09 (−CH$_2$−), 61.70, 117.87, 117.95, 120.56, 120.94, 124.54, 127.87, 127.95, 128.57, 129.39, 129.63, 129.72, 132.02, 136.12, 136.19, 136.47, 138.36, 143.65, 143.80, 155.04 (Ar−C), 188.57, 188.75 (CO). MS (EI): 596.82 [M]$^+$. HRMS: calcd for $C_{32}H_{26}Cl_2N_6O_2$, 596.1494; found, 596.1483.

3.1.1.7. N,N′-Bis(2-(4-bromophenylazo)-2-(4-chlorobenzoyl)vinyl)ethane-1,2-diamine (3e). Yellow crystals, mp 144−145 °C; IR (KBr) ν/cm$^{−1}$: 3208, 2927, 1633, 1580, 1475, 1269; ^{1}H NMR (DMSO-d_6): δ 3.87 (s, 2H, CH$_2$), 3.96 (s, 2H, CH$_2$), 6.79−6.81 (m, 2H, Ar−H, and CH = N), 7.22−7.24 (m, 2H, Ar−H), 7.47−7.62 (m, 8H, Ar−H), 7.77−7.78 (m, 2H, Ar−H), 7.87−7.88 (m, 2H, Ar−H), 8.20−8.23 (m, 2H, CH═N, Ar−H), 12.49 (b, 2H, NH); ^{13}C NMR (DMSO-d_6): δ 60.52, 61.15 (−CH$_2$−), 116.13, 116.22, 119.35, 119.88, 122.05, 122.41, 127.48, 128.18, 128.44, 131.51, 131.94,

135.20, 135.37, 135.47, 136.41, 137.15, 138.28, 142.35, 142.53, 148.10, 148.46, 150.66, 151.28 (Ar−C), 187.99, 189.28 (CO). MS (EI): 751.54 [M]$^+$. HRMS: calcd for $C_{32}H_{24}Br_2Cl_2N_6O_2$, 751.9704; found, 751.9699.

3.1.1.8. N,N′-Bis(2-(4-chlorophenylazo)-2-(4-bromobenzoyl)vinyl)ethane-1,2-diamine (3f). Orange crystals, mp 219−220 °C; IR (KBr) ν/cm$^{−1}$: 3416, 1642, 1585, 1531, 1489, 1257; ^{1}H NMR (DMSO-d_6): δ 3.86 (s, 2H, CH$_2$), 3.95 (s, 2H, CH$_2$), 6.80−7.08 (m, 1H, CH═N), 7.19 (d, J = 8.40 Hz, 2H, Ar−H), 7.28 (d, J = 8.40 Hz, 2H, Ar−H), 7.35 (d, J = 8.40 Hz, 1H, Ar−H), 7.45−7.63 (m, 11H, Ar−H), 8.17−8.21 (m, 1H, CH═N), 12.44 (b, 2H, NH); ^{13}C NMR (DMSO-d_6): δ 60.83 (−CH$_2$−), 119.04, 119.08, 121.75, 122.09, 126.28, 128.15, 128.85, 128.94, 129.10, 130.42, 131.05, 131.38, 131.69, 131.73, 132.12, 135.74, 136.37, 141.96, 148.09, 150.02, 151.30 (Ar−C), 188.16, 188.37 (CO). MS (EI): 472.10 [M]$^+$. HRMS: calcd for $C_{32}H_{24}Br_2Cl_2N_6O_2$, 751.9704; found, 751.9707.

3.1.1.9. N,N′-Bis(2-(4-chlorophenylazo)-2-(4-fluorobenzoyl)vinyl)ethane-1,2-diamine (3g). Yellow crystals, mp 197−198 °C; IR (KBr) ν/cm$^{−1}$: 3053, 2924, 1648, 1597, 1540, 1434, 1272; ^{1}H NMR (DMSO-d_6): δ 3.88 (s, 2H, CH$_2$), 3.97 (s, 2H, CH$_2$), 6.80 (d, J = 7.20 Hz, 2H, Ar−H, and CH═N), 7.27−7.45 (m, 5H, Ar−H), 7.46−7.54 (m, 3H, Ar−H), 7.56−7.76 (m, 5H, Ar−H), 8.15−8.22 (m, 3H, CH═N, Ar−H), 12.56 (b, 1H, NH), 12.60 (b, 1H, NH); ^{13}C NMR (DMSO-d_6): δ 60.55, 61.17 (−CH$_2$−), 114.25, 114.39, 114.98, 115.12, 122.03, 127.94, 128.04, 128.83, 129.04, 132.26, 136.50, 136.74, 141.99, 142.17, 148.01, 148.42, 150.32, 150.95, 163.60, 165.26 (Ar−C), 187.80, 188.00 (CO). MS (EI): 631.91 [M]$^+$. HRMS: calcd for $C_{32}H_{24}Cl_2F_2N_6O_2$, 632.1305; found, 632.1300.

3.1.1.10. N,N′-Bis(2-(4-bromophenylazo)-2-(4-fluorobenzoyl)vinyl)ethane-1,2-diamine (3h). Yellow crystals, mp 178−180 °C; IR (KBr) ν/cm$^{−1}$: 3057, 2899, 1647, 1597, 1542, 1490, 1440, 1270; ^{1}H NMR (DMSO-d_6): δ 3.88 (s, 2H, 2CH$_2$), 3.97 (s, 2H, CH$_2$), 6.80 (d, J = 7.20 Hz, 4H, Ar−H, and CH═N), 7.27−7.49 (m, 6H, Ar−H), 7.75−7.85 (m, 5H, Ar−H), 8.21−8.22 (m, 3H, CH═N, Ar−H), 12.61(b, 2H, NH); ^{13}C NMR (DMSO-d_6): δ 60.49, 61.11 (−CH$_2$−), 114.25, 114.39, 114.98, 115.12, 116.03, 119.31, 121.99, 122.36, 128.25, 131.80, 132.96, 133.02, 136.53, 136.78, 142.56, 148.08, 151.26, 163.60, 165.26 (Ar−C), 187.77, 187.97 (CO). MS

(EI): 721.66 $[M]^+$. HRMS: calcd for $C_{32}H_{24}Br_2F_2N_6O_2$, 722.0295; found, 722.0277.

3.1.1.11. N,N′-Bis(2-(4-bromophenylazo)-2-(4-methoxybenzoyl)vinyl)ethane-1,2-diamine (3i). Yellow crystals, mp 207–208 °C; IR (KBr) ν/cm^{-1}: 3003, 2927, 1634, 1601, 1541, 1487, 1438, 1258; ^{1}H NMR (DMSO-d_6): δ 3.84 (s, 6H, 2-OCH$_3$), 3.85 (s, 2H, CH$_2$), 3.97 (s, 2H, CH$_2$), 6.76–6.77 (m, 2H, Ar–H, and CH═N), 7.25–7.39 (m, 2H, Ar–H), 7.60–7.62 (m, 4H, Ar–H), 7.73–7.75 (m, 2H, Ar–H), 7.88–7.91 (m, 5H, Ar–H), 8.18–8.21 (m, 3H, CH═N, Ar–H), 12.72 (b, 1H, NH), 12.89 (b, 1H, NH); ^{13}C NMR (DMSO-d_6): δ 55.27, 55.44 (−OCH$_3$), 60.46, 61.06 (−CH$_2$−), 112.73, 113.44, 113.47, 115.66, 115.75, 119.00, 119.07, 122.18, 129.02, 129.09, 132.47, 136.99, 137.30, 142.52, 142.67, 148.07, 148.70, 150.32, 151.14, 161.34, 161.44 (Ar–C), 187.57, 187.77 (CO). MS (EI): 743.71 $[M]^+$. HRMS: calcd for $C_{34}H_{30}Br_2N_6O_4$, 744.0695; found, 744.0690.

3.1.1.12. N,N′-Bis(2-(4-chlorophenylazo)-2-(4-methoxybenzoyl)vinyl)ethane-1,2-diamine (3j). Yellow crystals, mp 190–191 °C; IR (KBr) ν/cm^{-1}: 3250, 2894, 1634, 1602, 1575, 1540, 1492, 1438, 1307; ^{1}H NMR (DMSO-d_6): δ 3.84 (s, 6H, 2OCH$_3$), 3.85 (s, 2H, CH$_2$), 3.97 (s, 2H, CH$_2$), 6.78 (s, 1H, CH═N), 6.87–7.05 (m, 3H, Ar–H), 7.20–7.36 (m, 8H, Ar–H), 7.45–7.68 (m, 2H, Ar–H), 7.81–7.90 (m, 2H, Ar–H), 8.16–8.21 (m, 2H, Ar–H, and CH═N), 12.85 (b, 2H, 2NH); ^{13}C NMR (DMSO-d_6): δ 55.27, 55.44 (−OCH$_3$), 60.53, 61.12 (−CH$_2$−), 112.72, 113.47, 118.72, 121.41, 121.84, 127.60, 127.69, 129.04, 130.85, 131.26, 132.04, 132.46, 136.97, 137.26, 142.12, 142.27, 147.99, 148.59, 150.04, 150.83, 161.43, 162.71 (Ar–C), 187.59, 187.79 (CO). MS (EI): 656.95 $[M]^+$. HRMS: calcd for $C_{34}H_{30}Cl_2N_6O_4$, 656.1705; found, 656.1700.

3.1.1.13. N,N′-Bis(2-(4-chlorophenylazo)-2-(benzoyl)vinyl)ethane-1,2-diamine (3k). Orange crystals, mp 196–197 °C; IR (KBr) ν/cm^{-1}: 3085, 3060, 2937, 1637, 1586, 1560, 1479, 1446, 1320; ^{1}H NMR (DMSO-d_6): δ 3.97 (s, 4H, 2CH$_2$), 7.17–7.19 (m, 1H, CH═N), 7.28–7.54 (m, 10H, Ar–H), 7.65–7.68 (m, 6H, Ar–H), 7.82–7.84 (m, 1H, Ar–H), 8.20–8.23 (m, 2H, Ar–H, and CH═N), 12.66 (b, 2H, 2NH); ^{13}C NMR (DMSO-d_6): δ 60.59, 61.21(−CH$_2$−), 118.91, 121.96, 127.36, 127.99, 128.80, 128.89, 129.04, 129.60, 130.04, 130.48, 132.30, 136.78, 136.86, 142.02 (Ar–C), 189.35 (CO). MS (EI): 595.73 $[M]^+$. HRMS: calcd for $C_{32}H_{26}Cl_2N_6O_2$, 596.1494; found, 596.1492. Crystal data: $C_{32}H_{26}Cl_2N_6O_2$, monoclinic, a = 11.0544 Å, b = 11.452 Å, c = 12.0243 Å, a = 90°, b = 100.751(7)°, g = 90°, V = 1495.5 Å^3, T = 296 K, space group: $P2_1/c$, Z = 4, calculated density = 1.327 g cm^{-3}, no. of refection measured 2621, theta (max) = 67.005, $R1$ = 0.0642.[77]

3.1.1.14. N,N′-Bis(2-(4-bromophenylazo)-2-(benzoyl)vinyl)ethane-1,2-diamine (3l). Orange crystals, mp 211–212 °C; IR (KBr) ν/cm^{-1}: 3067, 2924, 1637, 1597, 1597, 1486, 1446, 1262; ^{1}H NMR (DMSO-d_6): δ 3.80 (s, 2H, CH$_2$), 3.88 (s, 2H, CH$_2$), 6.80 (s, 4H, Ar–H, and CH═N), 7.21–7.31 (m, 9H, Ar–H), 7.75–7.85 (m, 5H, Ar–H), 8.21–8.22 (m, 2H, CH═N, Ar–H), 12.58 (b, 2H, NH); ^{13}C NMR (DMSO-d_6): δ 60.53, 61.15 (−CH$_2$−), 115.98, 116.06, 119.25, 119.62, 119.72, 121.92, 127.36, 128.01, 128.66, 129.61, 130.49, 130.63, 131.72, 131.90, 132.30, 142.42, 142.58, 148.45, 150.60, 162.27 (Ar–C), 189.32, 190.55 (CO). MS (EI): 684.32 $[M]^+$. HRMS: calcd for $C_{32}H_{26}Br^{81}Br$ N_6O_2, 684.0483; found, 684.0446.

3.1.1.15. N,N′-Bis(2-(2-nitrophenylazo)-2-(benzoyl)vinyl)ethane-1,2-diamine (3m). Yellow crystals, mp 235–236 °C; IR (KBr) ν/cm^{-1}: 3098, 3072, 2918, 1642, 1607, 1576, 1446, 1419, 1277; ^{1}H NMR (DMSO-d_6): δ 3.87 (s, 2H, CH$_2$), 3.96 (s, 2H, CH$_2$), 6.79 (s, 1H, CH═N), 7.19–7.21 (m, 1H, Ar–H), 7.29–7.31 (m, 1H, Ar–H), 7.35–7.38 (m, 4H, Ar–H), 7.41–7.47 (m, 4H, Ar–H), 7.61–7.71 (m, 5H, CH═N, Ar–H), 7.79 (d, 2H, CH═N, Ar–H), 8.18–8.22 (m, 2H, CH═N, Ar–H), 12.51 (b, 2H, NH); ^{13}C NMR (DMSO-d_6): δ 60.61, 61.23(−CH$_2$−), 119.03, 121.73, 122.07, 124.14, 124.30, 126.20, 128.05, 128.38, 128.84, 129.05, 130.40, 131.03, 131.67, 132.11, 135.73, 136.36, 136.59, 138.31, 138.67, 141.95, 142.12, 148.04, 148.37, 150.35, 150.94, 157.34 (Ar–C), 188.15, 189.23 (CO). MS (EI): 618.01 $[M]^+$. HRMS: calcd for $C_{32}H_{26}N_8O_6$, 618.1975; found, 618.1977.

3.1.1.16. N,N′-Bis(2-(4-tolylazo)-2-(2-thienoyl)vinyl)ethane-1,2-diamine (3n). Yellow crystals, mp 158–160 °C; IR (KBr) ν/cm^{-1}: 3082, 3063, 2927, 1615, 1592, 1547, 1433, 1277; ^{1}H NMR (DMSO-d_6): δ 2.29 (s, 6H, 2CH$_3$), 3.96 (s, 4H, 2CH$_2$), 7.15–7.21 (m, 4H, Ar–H and CH═N), 7.58 (d, 2H, J = 9.60 Hz, Ar–H), 7.93–7.94 (m, 4H, Ar–H), 7.99–8.00 (m, 4H, Ar–H), 8.24–8.27 (m, 2H, Ar–H and CH═N), 12.73 (b, 1H, NH), 12.76 (b, 1H, NH); ^{13}C NMR (DMSO-d_6): δ 51.98 (−OCH$_3$), 61.45 (−CH$_2$−), 118.36, 120.40, 120.72, 121.10, 126.87, 126.96, 127.81, 128.31, 129.56, 129.63, 133.52, 133.79, 134.69, 134.69, 135.96, 136.83, 137.07, 138.56, 140.10, 141.28, 148.40, 148.78 (Ar–C), 178.91, 179.70 (CO). MS (EI): 567.99 $[M]^+$. HRMS: calcd for $C_{30}H_{28}N_6O_2S_2$, 568.1715; found, 568.1710.

3.1.1.17. N,N′-Bis(2-(phenylazo)-2-(2-thienoyl)vinyl)ethane-1,2-diamine (3o). Yellow crystals, mp 263–264 °C; IR (KBr) ν/cm^{-1}: 3101, 3072, 2897, 1629, 1597, 1547, 1465, 1414, 1274; ^{1}H NMR (DMSO-d_6): δ 3.99 (s, 4H, 2CH$_2$), 6.82 (s, 1H, CH═N), 7.18–7.24 (m, 6H, Ar–H), 7.43–7.53 (m, 3H, Ar–H), 7.66 (d, J = 7.80 Hz, 3H, Ar–H), 7.92–8.05 (m, 3H, Ar–H), 8.32 (d, J = 9.60 Hz, 2H, Ar–H), 12.97 (b, 2H, NH); ^{13}C NMR (DMSO-d_6): δ 61.20, 61.85 (−CH$_2$−), 118.01, 118.17, 120.67, 121.08, 124.19, 126.92, 127.76, 128.88, 129.28, 133.66, 134.80, 136.70, 138.50, 140.18, 140.39, 143.51, 147.63, 148.01, 151.19 (Ar–C), 179.05, 179.20 (CO). MS (EI): 540.10 $[M]^+$. HRMS: calcd for $C_{28}H_{24}N_6O_2S_2$, 540.1402; found, 540.1404.

4. CONCLUSIONS

Due to the involvement of bis-amines in a wide-array of highly promising biologically active candidates, this work describes an interesting platform for the construction of novel *N,N′*-bis(2-(arylazo)-2-(aroyl)vinyl)ethane-1,2-diamines. These targets were assembled based on the reaction of ethylenediamine with various 2-arylhydrazono-3-oxopropanals in aqueous conditions under both conventional stirring and MW conditions at ambient temperature. The optimal reaction condition was found to be a mixture of methanol/H$_2$O (2:1). The structures of the new products were established from their elemental and spectroscopic analyses as well as X-ray single crystals of a demonstrative compound. The photophysical behavior of the bis-arylazo derivatives, having various substituents of different electronic behaviors, was studied. The UV−vis spectra in dichloromethane solution showed the maximum absorption band in the range of 348−383 nm due to $n \rightarrow \pi^*$ and/or $\pi \rightarrow \pi^*$ electronic transitions of azo chromophores with molar extinction coefficients ranging from 0.89×10^4 to 4.02×10^4 M^{-1} cm^{-1}. The highest molar

absorptivity coefficient ($\sim 45 \times 10^3$ M^{-1} cm^{-1}) was observed in CHCl$_3$ solvent. The fluorescence properties in DMSO showed that the emission maximum emerges in the visible region in the 389−441 nm range. Some compounds were considered interesting fluorophore materials by showing high Stokes shifts. The PL study of some compounds was promising, with maximal emission peaks ranging between 417−436 nm.

■ ASSOCIATED CONTENT

Data Availability Statement

The data supporting this article have been included as part of the Supporting Information.

ⓈⒾ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c06250.

^{1}H NMR; ^{13}C NMR; HRMS; and MS of compounds (PDF)

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Author Contributions

A.A. conceived the project and directed the research. A.A., K.D., and M.H. designed the experiments. W.T. conducted the experiments. A.A., K.D., and W.T. analyzed the data and wrote the manuscript. A.A., K.W., and H.M. discussed the results and edited the manuscript.

Notes

The authors declare no competing financial interest.

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