Catalyst-Free and Green Synthesis of Some Novel Benzamide Derivatives

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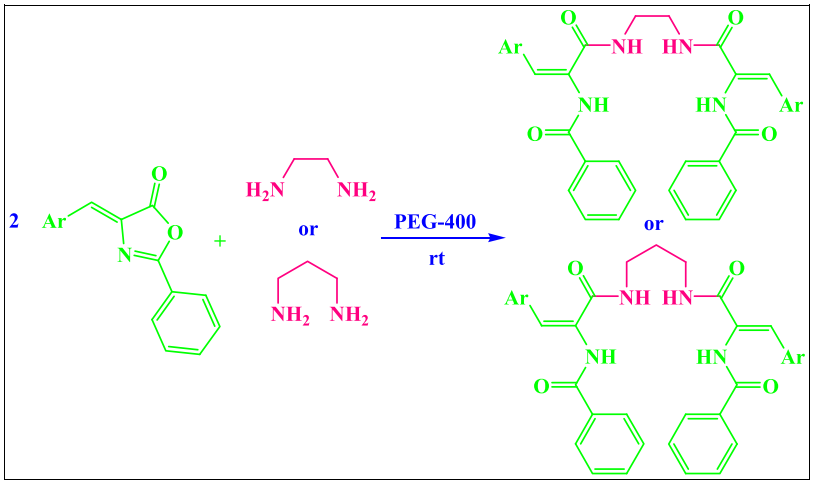


In the present work, a simple, green, rapid, and catalyst-free procedure for the synthesis of benzamide derivatives by ring opening of azlactones with diamines such as ethylene diamine and 1,3-propylenediamine is described. The present method offers several advantages such as short reaction times, easy work-up, and mild reaction conditions in the absence of catalyst and any toxic solvent and material. In addition, the structure obtained by X-ray crystallography was compared with the theoretical results obtained by density functional theory using the B3LYP functional and cc-pVDZ basis sets.

INTRODUCTION

It is well accepted that amide groups are not only the key chemical connection of biological systems but are also the basis for some of the most versatile and widely used synthetic polymers [1]. In addition, anti-retroviral drugs such as HIV-1 NCp7 inhibitors [2], anti-inflammatory, antipyretic, analgesic activities, treatment of atherosclerosis [3], inhibitors of hepatitis C [4], and inhibitors for targeted melanoma therapy [5] are remarkable properties of these compounds. Amide group is prepared via different methods such as reaction between primary amine and acyl chloride [6–8], nucleophilic attack to isothiocyanate [9], one-pot condensation of an aldehyde, acetyl chloride, an enolizable ketone and acetonitrile [10], condensation of carboxylic acids with amines in the presence of nanosized sulfated titania [11], and ring-opening of azlactones with amines [12–14]. Recently, primary amides were synthesized directly from primary alcohols and ammonia using manganese oxide based octahedral molecular sieve (OMS-2) as a heterogeneous catalyst [15].

These nitrogen-containing compounds play a critical role in biological applications, and they provide a valuable modeling for such applications [16]. In fact, the routes listed are valuable, but the use of toxic material and solvents, high temperatures, long reaction times, low yields, and multiple steps for separation could be considered as disadvantages of these methods.

Poly(ethylene glycol)s (PEGs) are used as eco-friendly solvents and can be applied instead of volatile or halogenated organic solvents. These are non-flammable, non-corrosive, benign, and readily commercially available at low cost [17]. The PEGs are amphipathic polymers that are able to dissolve common organic solids [18], and they present some interesting characteristics, including high polarity and high boiling point. Moreover, PEGs are stable to acidic or basic, oxidative or reductive conditions and at high temperatures (up to 150–250°C). PEGs with low molecular weight (less than 800 Da) are viscous liquids at room temperature and can therefore be used as suitable liquid media [19].

Peptides play vital roles in the human body and other organisms [20]. Because of the good affinity of peptides toward cells and nucleic acids, the introduction of a peptide segment to drugs can facilitate their actions to cells and tissues and thereby provide a robust strategy to design new

drugs or lead compounds. On the other hand, heterocyclic compounds have distinguished themselves from other small molecules because of their profound bioactivities. The practice of ring opening of heterocyclic skeletons with another amine group into one molecule has received much attention from synthetic and medicinal chemists for the discovery of novel compounds with unknown or improved pharmacological properties [21].

Because of the importance of amide compounds, we decided to synthesize a new class of these compounds as potent drugs by the ring-opening of azlactones with ethylene diamine and 1,3-propyldiamine under catalyst-free conditions using PEG-400 as reaction medium at room temperature (Scheme 1). The second aim of this work was the application of these amides as ligand for coordination with metals.

RESULTS AND DISCUSSION

Synthesis of amide compounds. First, the reaction conditions were optimized in the reaction of (4*Z*)-4-(4-bromobenzylidene)-2-phenyloxazol-5(4*H*)-one with ethylene diamine. For choosing the reaction media, the model reaction was carried out in methanol, ethanol, acetonitrile, DMF, DMSO, and PEG-400 and also under solvent-free conditions. As can be seen, the highest yield was obtained at PEG-400; therefore, all reactions were performed in this solvent. As mentioned previously, the exact role of PEG-400 in this reaction is not clear [22]. Further studies showed that a 2:1 ratio of azlactone to ethylene diamine is the best. Because the model reaction was carried out efficiently at room temperature, therefore, room temperature was chosen as reaction temperature. When the model reaction was carried out at 50°C, the reaction time was reduced to 8 min (Table 1).

Under the optimized reaction conditions, the reaction of different azlactone derivatives with ethylene diamine was carried out under catalyst-free conditions at room temperature. The results, which are summarized in Table 2, showed that the corresponding amides were obtained in high to excellent yield. It seems that the nature of the substituents on the aromatic ring has no significant effect on the reaction yield. Under the same conditions described for the reaction of ethylene diamine with azlactones, the reaction of 1,3-diaminopropane was also investigated (Table 3), and the corresponding amide compounds were produced in high to excellent yield.

When 1,2-phenylenediamine was used as diamine in the reaction of compound **1d**, the corresponding amide **4d** was produced in 75% yield (Scheme 2).

Scheme 3 shows the proposed mechanism for these reactions. First, diamine reacts with one azlactone molecule **1** to give the intermediate **I**, which in turn gives the compounds **II** and **III**. The free amine in compound **III** reacted with another azlactone molecule **1** to give the intermediate **IV**, which is converted to compound **V** and then to final product **2**.

The structures of all compounds were ascertained by elemental analysis and spectral (IR, UV–vis, ^{1}H NMR, and ^{13}C NMR) data. Furthermore, the structure of compound **3b** was confirmed by X-ray crystallographic analysis (CCDC 908176, Fig. 1). Note that a water molecule is present in the crystal structure. Also, the crystal packing of this compound is shown in Figure 2.

In the next step, we tried to coordinate these amide compounds as a four-dentate ligand to different metals such as Mn, Fe, Co, Cu, Zn, Ru, Rh, Pt, and Pd. After several attempts, no complex was formed, and except for Pd, the amide ligand was recovered from the reaction mixture. Addition of a base such as K_2CO_3, NaOH, and NaH and increasing the temperature give no better results. Surprisingly, in the case of Pd, the amide ligand was cleaved to its azlactone parent.

As shown in Table 4, different amide compounds were converted to their corresponding azlactones in the presence of $PdCl_2$ or $Pd(OAc)_2$ at room temperature. Unfortunately, we could not find any reason for this reaction.

Computational methods. Density functional theory (DFT) using the B3LYP functional and cc-pVDZ basis sets were carried out for geometry optimization and electronic properties of compound **3b**, whereas the

Scheme 1

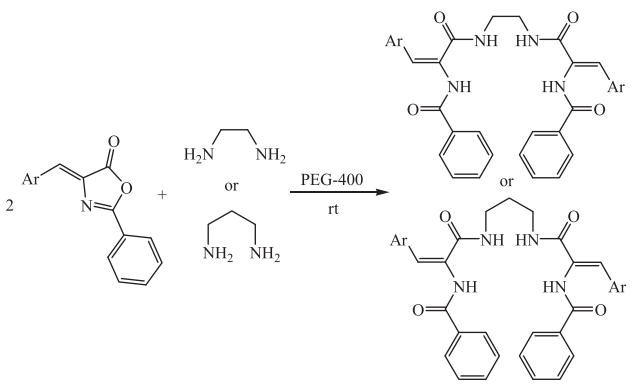


Table 1

The effect of solvent on the reaction of (4*Z*)-4-(4-bromobenzylidene)-2-phenyloxazol-5(4*H*)-one (**2g**) with ethylene diamine.[a]

Entry	Solvent	Time (min)	Yield (%)[b]
1	No solvent	12	62
2	Ethanol	12	80
3	Methanol	12	75
4	Acetonitrile	12	67
5	DMF	12	71
6	DMSO	12	82
7	PEG-400	12	93

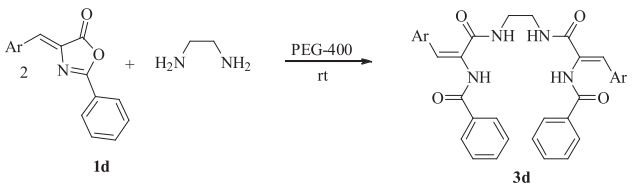
[a]Reaction conditions: azlactone (2 mmol), ethylene diamine (1 mmol), solvent (1 mL) at room temperature.
[b]Isolated yield.

electronic transition energies and oscillator strengths were determined by the TD-DFT/cc-pVDZ level of theory. All calculations were performed using the Turbomole program package [23]. The X-ray experimental data were used for starting geometry in calculations. The optimized geometry parameters are listed in Table 5 along with experimental results obtained from X-ray crystallographic study.

Ground state optimized geometry parameters. The optimized structure and the numbering pattern of compound **3b** are represented in Figure 3. From the structural data in Table 5, comparing the X-ray geometric parameters to corresponding optimized parameters (Fig. 3), slight differences are observed. The most important miss matching is related to the torsion angles C18–C19–N3–C20, C17–C18–C19–N3 and N3–C20–C21–N4, which were obtained in this work as −71.12°, −66.652°, and −138.82, and their experimental values are −90.6°, −85.35° and −154.3, respectively. The optimized structure shows the existence of hydrogen bond between the N—H…O, namely N3—H3 and N2—H2 with O1 and O4

Table 2

Synthesis of benzamide derivatives by the reaction of azlactones with ethylene diamine.[a]

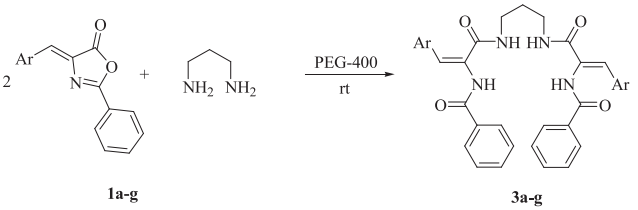


Entry	Ar	Yield (%)[b]	Time (min)
1	**a**	90	10
2	**b**	94	15
3	**c**	94	15
4	**d**	95	10
5	**e**	94	10
6	**f**	93	12
7	**g**	88	20

[a]Reaction conditions: azlactone (2 mmol) and ethylene diamine (1 mmol).
[b]Isolated yield.

Table 3

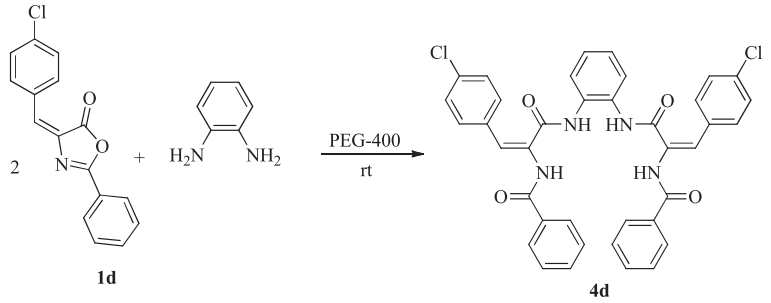
Synthesis of benzamide derivatives by the reaction of azlactones with 1,3-propanediamine.[a]



Entry	Ar	Yield (%)[b]	Time (min)
1	**a**	92	10
2	**b**	92	15
3	**c**	95	10
4	**d**	94	10
5	**e**	94	8
6	**f**	90	15
7	**g**	90	15

[a]Reaction conditions: azlactone (2 mmol) and 1,3-diaminopropane (1 mmol).
[b]Isolated yield.

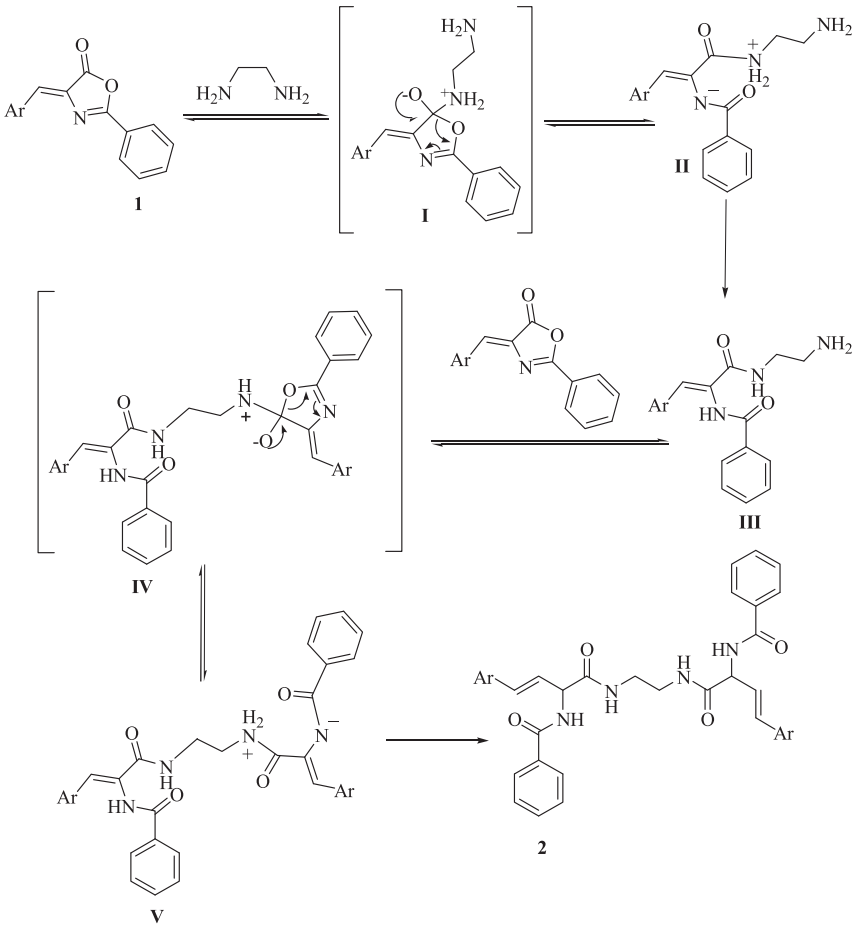
Scheme 2



atoms, respectively, in which stronger interaction observed in the view of DFT/cc-pVDZ level of calculation in comparison with X-ray. The presence of the H-bond shows an important role in the stabilization of molecular conformations. The other structural parameters remained unchanged or showed no considerable change.

Electronic absorption spectra (comparison between theoretical and experimental results). Simulated absorption spectra in gas and in ethanol using Conductor-like Screening Model (COSMO) [24–26] were taken and along with its experimental results are displayed in Figure 4. In order to obtain the theoretical spectrum, 30 vertically singlet-excitations were used for calculation. The results are presented in Table 6. The UV–Vis spectrum of compound **3b** in ethanol (Fig. 4) shows a sharp peak at 330 nm as λ_{max} and a shoulder at 230 nm. Although theoretical transition energies have excellent agreement with the experimental spectrum, it seems the electrostatic solvent interactions (COSMO model) lead to slightly red-shift effect on transition energies. Also, that is accompanied

Scheme 3



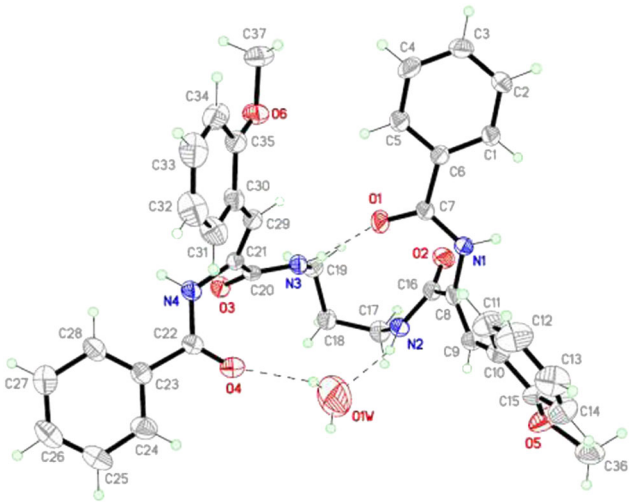


Figure 1. The crystal structure of compound **3b**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with slightly alteration of orbital contributions. Obviously, the polar solvent mostly affects the orbital energy gaps too.

As shown in Table 7, considering the oscillator strength, there are several intense electronic transitions. The first one is a $\pi\pi^*$ (H-1 → L) transition, which lies at the 3.75 eV (330.93 nm) in gas phase and 3.74 eV (331.93 nm) in solvent (Table 7). On the other hand, there are several weak transitions; among them, S_{10} (2.95 eV) in gas and S_{11} (4.34 eV) in solvent are more intense than the others. The single-electron excitations that correspond to these two transitions are H → L + 3 and H-1 → L + 2 in the gas phase and in solvent, respectively (Fig. 5).

In conclusion, an efficient method for preparation of amide derivatives by the reaction of diamines with azlactones under catalyst-free conditions is described. On the other hand, their conversion to their parent azlactones in the presence of Pd salts was studied. Finally, the obtained results by X-ray crystallography were compared with the theoretical results, and a good adaptation was observed.

EXPERIMENTAL

Chemicals and reagents. All reagents were obtained from the commercial sources and used as received. FT-IR spectra were obtained as potassium bromide pellets in the range of 400–4000 cm^{-1} with a Nicolet Impact 400D instrument. UV–Vis spectra were recorded on a JASCO V-670 spectrophotometer. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on Bruker-Avance 400 using DMSO-d_6 as solvent. Elemental analysis was carried out on a LECO, CHNS-932 instrument. Azlactones were prepared according to published procedure [27].

General procedure for preparation of amides. In a 25-mL round bottom flask, a solution of PEG (PEG-400, 1 mL) and azlactone (2 mmol) was stirred. Then, ethylene diamine or 1,3-diaminopropane (1 mmol) was added to the reaction mixture, and the mixture was stirred for 30 min at room temperature. During this time, the color of the solution gradually changed to colorless. The reaction progress was monitored by TLC (petroleum ether/ethyl acetate: 1/1). After the reaction was completed, distilled water (5 mL) was added. The white precipitates were centrifuged, dried, and recrystallized from hot ethanol.

General procedure for reaction of amides with metal salts of Mn, Fe, Co, Cu, Zn, Ru, Rh, Pt, and Pd. In a 25-mL round bottom flask, a solution of amide (1 mmol) in ethanol (10 mL) was prepared. A solution of metal salt in ethanol (10 mL) was added to this solution, and the reaction mixture was stirred at room temperature or at 60°C. At the end of the reaction, the solvent was evaporated to obtain the reaction product.

Supporting information

N,N′-(1E,1′E)-3,3′-(Ethane-1,2-diylbis(azanediyl))bis(3-oxo-1-(thiophen-2-yl)prop-1-ene-3,2-diyl)dibenzamide (2a). mp 153–155°C; IR (KBr): ν (cm^{-1}): 3324, 3267, 3067, 2931, 1645, 1527, 1473, 1271, 1233, 1209, 716, 626. ^1H NMR (400 MHz, DMSO-

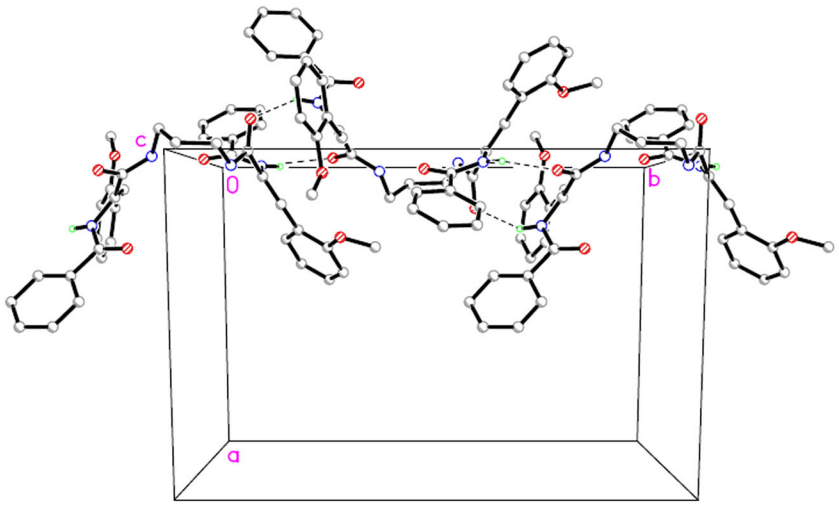
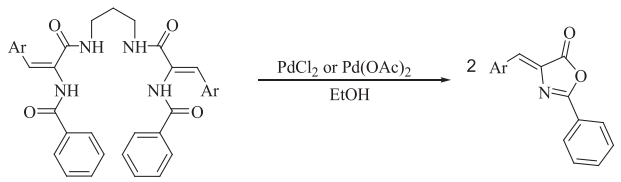
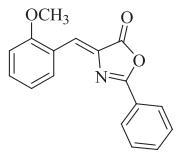
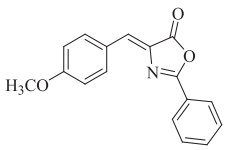
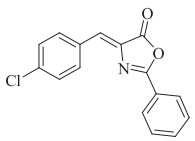
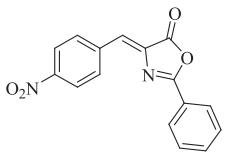
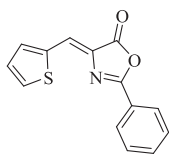


Figure 2. The crystal packing of compound **3b**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

Table 4

Cleavage of amide compounds to azlactones in the presence of palladium salts.[a]



Entry	Product	Yield (%)[b]	Time (min)
1		92	10
2		90	10
3		93	5
4		87	12
5		90	8

[a]Reaction conditions: amide compound (1 mmol), Pd salt (1 mmol), and EtOH (20 mL).
[b]Isolated yield.

d_6), δ: 9.80 (s, 2H, N—H Benzamide), 8.28 (s, 2H, N—H amide), 8.09 (d, $J = 7.2$ Hz), 7.66 (s, H-benzyl), 7.61–7.64 (m, 2H), 7.52–7.59 (m, 4H), 7.39 (d, $J = 2.8$ Hz), 7.1 (dd, $^1J = 5.2$, $^2J = 3.6$ Hz), 3.38 (s, 4H, CH_2—CH_2). ^{13}C NMR (100 MHz, DMSO-d_6), δ: 39.0, 125.6, 126.6, 126.8, 128.1, 128.2, 130.2, 131.6, 132.2, 133.9, 135.7, 164.7, 165.0. $C_{30}H_{26}N_4O_4S_2$ Calcd: C, 63.14%; H, 4.59%; N, 9.82%; S, 11.24%; Found: C, 63.09%; H, 4.62%; N, 9.78%, S, 11.20%. UV–vis (λ_{max}, nm): 319.

Table 5

Experimental and optimized structural parameter results.

Parameters	DFT cc-pVDZ	Experimental
	Bond lengths (Å)	
C1–C2	1.397	1.381(5)
C2–C3	1.398	1.374(6)
C3–C4	1.400	1.376(6)
C4–C5	1.395	1.372(5)
C5–C6	1.404	1.387(5)
C6–C1	1.405	1.383(5)
C6–C7	1.500	1.501(4)
C7–O1	1.231	1.222(4)
C7–N1	1.374	1.350(4)
N1–C8	1.407	1.441(5)
C8–C16	1.517	1.461(6)
C16–O2	1.228	1.246(4)
C16–N2	1.360	1.358(4)
N2–C17	1.459	1.472(5)
C17–C18	1.535	1.510(6)
C18–C19	1.540	1.549(5)
C19–N3	1.460	1.447(5)
N3–C20	1.355	1.310(5)
C20–O3	1.229	1.258(4)
C20–C21	1.518	1.495(5)
C21–N4	1.408	1.423(4)
N4–C22	1.375	1.365(4)
C22–O4	1.231	1.206(5)
C22–C23	1.501	1.493(6)
C23–C28	1.405	1.337(6)
C28–C27	1.397	1.444(6)
C27–C26	1.398	1.355(6)
C26–C25	1.400	1.350(7)
C25–C24	1.395	1.376(6)
C24–C23	1.404	1.387(5)
N4–C21	1.408	1.423(4)
C21–C29	1.353	1.339(4)
C29–C30	1.469	1.464(5)
C30–C31	1.424	1.374(6)
C31–C32	1.398	1.375(6)
C32–C33	1.395	1.370(7)
C33–C34	1.400	1.365(7)
C34–C35	1.400	1.396(6)
C35–C30	1.424	1.422(5)
C35–O6	1.365	1.369(5)
O6–C37	1.419	1.425(4)
C8–C9	1.354	1.340(5)
C9–C10	1.470	1.449(6)
C10–C11	1.407	1.398(6)
C11–C12	1.398	1.379(7)
C12–C13	1.395	1.347(7)
C13–C14	1.400	1.378(7)
C14–C15	1.400	1.387(6)
C15–O5	1.364	1.374(5)
O5–C36	1.419	1.413(6)
C15–C10	1.423	1.386(6)
O1–H3B	1.944	2.084
O4–H2B	2.027	4.430
	Bond angles (°)	
N2–C17–C18	113.963	113.5(4)
C17–C18–C19	116.023	113.7(3)
C18–C19–N3	113.867	114.1(3)
C19–N3–C20	120.357	122.1(3)

(Continued)

Table 5
(*Continued*)

Parameters	DFT cc-pVDZ	Experimental
N3–C20–O3	124.43	121.6(4)
C20–C21–N4	113.971	114.2(3)
C21–C22–N4	124.032	120.2(3)
N4–C21–C29	123.799	121.3(4)
C29–C30–C31	124.007	125.2(3)
C30–C31–C32	121.924	123.5(4)
C32–C33–C34	120.221	121.6(3)
C34–C35–C30	120.775	121.4(4)
C34–C35–O6	123.707	123.8(4)
C35–O6–C37	118.88	117.9(4)
N4–C22–O4	122.663	122.1(4)
O4–C22–C23	121.456	121.5(3)
C22–C23–C28	123.071	123.8(4)
C23–C28–C27	120.297	120.7(4)
C28–C27–C26	120.076	117.7(5)
C27–C26–C25	119.884	121.2(5)
C26–C25–C24	120.105	121.1(5)
C24–C23–C28	120.367	119.8(4)
C17–N2–C16	121.061	124(4)
N2–C16–O2	124.905	121.4(4)
O2–C16–C8	119.991	123.2(3)
C8–N1–C7	115.081	118.7(3)
N1–C7–O1	122.774	122.2(3)
C7–C6–C1	117.657	123.1(4)
C1–C2–C3	120.328	119.8(4)
C2–C3–C4	120.122	121(3)
C3–C4–C5	119.885	118.8(4)
C4–C5–C6	120.081	121.3(4)
C8–C9–C10	128.39	130.1(3)
C9–C10–C11	123.692	122.8(4)
C9–C10–C15	118.686	121.1(4)
C10–C15–C14	120.718	122.1(4)
C15–C14–C13	120.038	118.8(5)
C13–C12–C11	119.552	119.3(5)
C11–C10–C15	117.565	116(4)
C15–O5–C36	118.858	118.4(4)
	Dihedral angles (°)	
N3–C19–C18–C17	−71.12	−90.6(5)
C18–C19–N3–C20	−66.652	−85.35(4)
C19–N3–C20–O3	−7.08	4.2(5)
C20–C21–C29–C30	176.11	173.3(4)
N3–C20–C21–N4	−138.82	−154.3(3)
N2–C16–C8–C9	46.59	44.7(6)
C16–C8–C9–10	175.20	177.2(4)
C9–C8–N1–C7	−146.84	−139.7(4)
C19–C18–C17–N2	58.41	56.6(5)

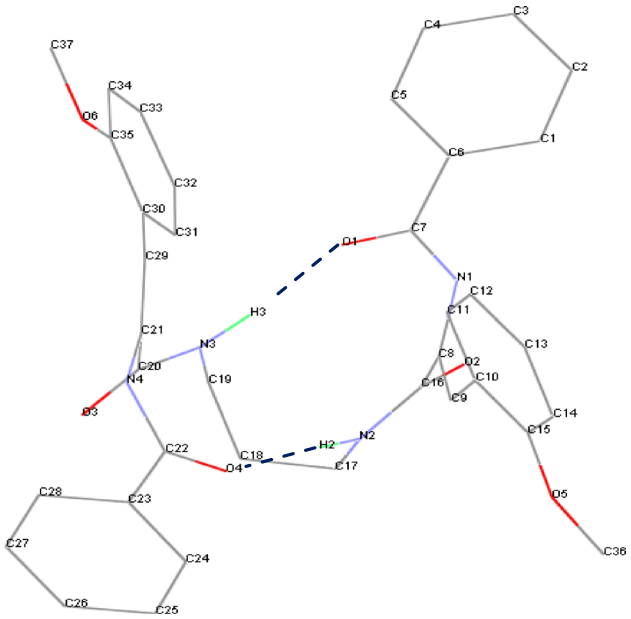


Figure 3. Optimized structure and their atom numbering of the title compound (hydrogen atoms clearly omitted except for hydrogen bonding). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

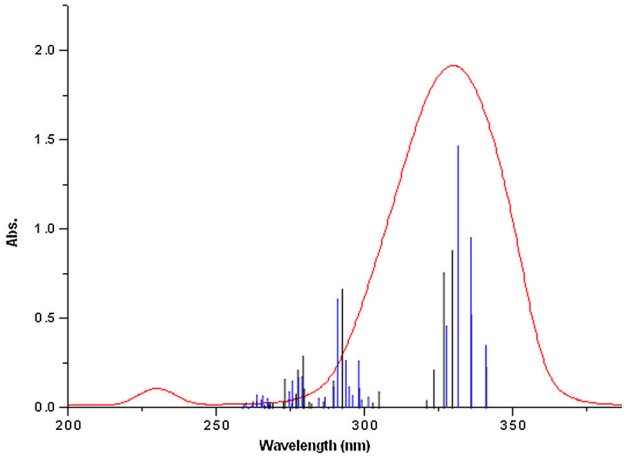


Figure 4. The experimental spectra of title compound with vertical excitation in gas phase (black lines) and in solvent (blue lines). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

N,N′-(1E,1′E)-3,3′-(Ethane-1,2-diylbis(azanediyl))bis(1-(2-methoxyphenyl)-3-oxoprop-1-ene-3,2-diyl)dibenzamide (2b). mp 228–230°C; IR (KBr): ν (cm^{-1}): 3393, 3343, 3285, 3239, 3063, 2838, 1648, 1617, 1577, 1519, 1480, 1253, 1021, 755, 706. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 9.80 (s, 2H, N—H Benzamide), 8.25 (s, 2H, N—H amide), 7.42–7.56 (m, 10H), 7.28 (td, 2H, ^1J = 15.6, ^2J = 1.2 Hz), 7.04 (d, 2H, J = 8.0 Hz), 6.84 (t, J = 7.6 Hz, 2H, Benzilic), 3.83 (s, 6H, O—CH_3), 3.3 (s, 4H, CH_2—CH_2). ^{13}C NMR (100 MHz, DMSO-d_6), δ: 24.4, 55.4, 111.1, 120.1, 123.9, 123.9, 127.9, 128.1, 128.5, 130.0, 131.4, 133.8, 157.1, 165.3, 165.9, 174.3. $C_{36}H_{34}N_4O_6$ Calcd: C, 69.89%; H, 5.54%; N, 9.06%; Found: C, 69.86%; H, 5.55%; N, 9.04%. UV–vis (λ_{max}, nm): 321.

N,N′-(1E,1′E)-3,3′-(Ethane-1,2-diylbis(azanediyl))bis(1-(4-methoxyphenyl)-3-oxoprop-1-ene-3,2-diyl)dibenzamide (2c). mp 137–140°C; IR (KBr): ν (cm^{-1}): 3371, 3296, 3057, 2940, 2840, 1647, 1609, 1577, 1536, 1508, 1473, 1258, 1207, 1176, 1024, 835, 704. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 9.87 (s, 2H, N—H Benzamide), 8.21 (s, 2H, N—H amide), 8.02 (d, 4H, J = 7.2 Hz), 7.58 (t, J = 7.6 Hz), 7.48–7.51 (8H, m), 7.20 (s, 2H, Benzilic), 6.90 (d, 4 Hz, J = 9.2 Hz), 3.74 (s, 6H, OCH_3), 3.29 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6), δ: 41.1, 55.1, 113.9,

Table 6

The calculated singlet excited states.

	Gas			Solvent		
State	Energy (eV)	Wavelength (nm)	Oscillator strength	Energy (eV)	Wavelength (nm)	Oscillator strength
S_1	3.62	342.86	0.050	3.62	342.76	0.084
S_2	3.67	337.62	0.115	3.68	336.90	0.231
S_3	3.75	330.93	0.195	3.74	331.93	0.355
S_4	3.78	327.99	0.167	3.79	327.42	0.110
S_5	3.82	324.54	0.047	4.17	297.32	0.014
S_6	3.85	321.95	0.010	4.21	294.66	0.009
S_7	4.06	305.31	0.020	4.22	293.65	0.063
S_8	4.09	303.15	0.007	4.26	291.18	0.015
S_9	4.15	298.40	0.024	4.28	289.75	0.028
S_{10}	4.24	292.47	0.147	4.30	288.64	0.063
S_{11}	4.28	289.37	0.034	4.34	285.35	0.147
S_{12}	4.31	287.65	0.000	4.37	283.76	0.027
S_{13}	4.34	285.88	0.008	4.42	280.50	0.013
S_{14}	4.40	281.74	0.005	4.46	278.08	0.012
S_{15}	4.41	280.92	0.008	4.56	271.73	0.041
S_{16}	4.44	279.17	0.023	4.59	270.28	0.040
S_{17}	4.45	278.77	0.064	4.63	267.89	0.035
S_{18}	4.48	276.98	0.047	4.65	266.72	0.020
S_{19}	4.49	276.28	0.017	4.78	259.52	0.003
S_{20}	4.51	274.98	0.006	4.79	258.79	0.002
S_{21}	4.55	272.39	0.035	4.80	258.26	0.012
S_{22}	4.56	271.95	0.007	4.83	256.53	0.015
S_{23}	4.62	268.20	0.006	4.85	255.80	0.009
S_{24}	4.64	267.23	0.007	4.88	254.22	0.016
S_{25}	4.65	266.82	0.004	4.88	254.14	0.008
S_{26}	4.65	266.67	0.007	4.91	252.64	0.007
S_{27}	4.67	265.51	0.001	4.91	252.39	0.002
S_{28}	4.67	265.30	0.004	4.92	252.00	0.001
S_{29}	4.78	259.57	0.000	4.96	249.87	0.005
S_{30}	4.81	257.66	0.000	4.98	249.02	0.003

Table 7

Calculated vertical transition energies at TD-DFT/cc-pVDZ level of theory on the optimized equilibrium geometry in gas phase and in solvent along with experimental results.

	Experimental		TD-DFT/cc-pVDZ		TD-DFT/cc-pVDZ/COSMO		
State	Wavelength (nm)	Abs.	Wavelength (nm)	Oscillator strength	Wavelength (nm)	Oscillator strength	Orbital contribution
S_3	330	2.00	331	0.20	331.9	0.35	H-1 → L
S_{10}	230	0.15	292.5	0.15	288.64	0.063	H → H + 3
S_{11}	—	—	289.37	0.034	285.4	0.15	H-1 → L + 2

126.6, 126.7, 127.7, 127.9, 128.2, 128.3, 128.8, 129.3, 131.0, 131.6, 133.7, 159.5, 165.5, 165.8. $C_{36}H_{34}N_4O_6$ Calcd: C, 69.89%; H, 5.54%; N, 9.06%; Found: C, 69.86%; H, 5.56%; N, 9.08%. UV–vis (λ_{max}, nm): 320.

N,N′-(1E,1′E)-3,3′-(Ethane-1,2-diylbis(azanediyl))bis(1-(4-chlorophenyl)-3-oxoprop-1-ene-3,2-diyl)dibenzamide (2d). mp 138–140°C (decomp.); IR (KBr): ν (cm^{-1}): 3365, 3266, 3067, 2963, 2874, 1654, 1609, 1543, 1483, 1280, 1091, 711. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 9.96 (s, 2H, N—H Benzamide), 8.31 (s, 2H, N—H amide), 7.97 (d, 4H, J = 11.6 Hz), 7.46–7.59 (m, 10H), 7.41 (d, 4H, J = 8.8 Hz), 7.16 (s, 2H, Benzilic), 3.34 (4H, CH_2—CH_2). ^{13}C NMR (100 MHz, DMSO-d_6), δ: 18.5, 56.0, 127.9, 128.2, 128.5, 130.6, 132.9, 165.2. $C_{34}H_{28}Cl_2N_4O_4$ Calcd: C, 65.08%; H, 4.50%; N, 8.93%; Found: C, 65.05%; H, 4.52%; N, 8.89%. UV–vis (λ_{max}, nm): 318.

N,N′-(1E,1′E)-3,3′-(Ethane-1,2-diylbis(azanediyl))bis(1-(2,4-dichlorophenyl)-3-oxoprop-1-ene-3,2-diyl)dibenzamide (2e). mp 128–130°C (decomp.); IR (KBr): ν (cm^{-1}): 3302, 3285, 3065, 2941, 2839.67, 1648, 1609.30, 1582, 1521, 1469, 1278, 1101, 1052, 868, 693. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 9.92 (s, 2H, N—H Benzamide), 8.40 (t, J = 5.2 Hz, 2H, N—H amide), 7.91 (d,

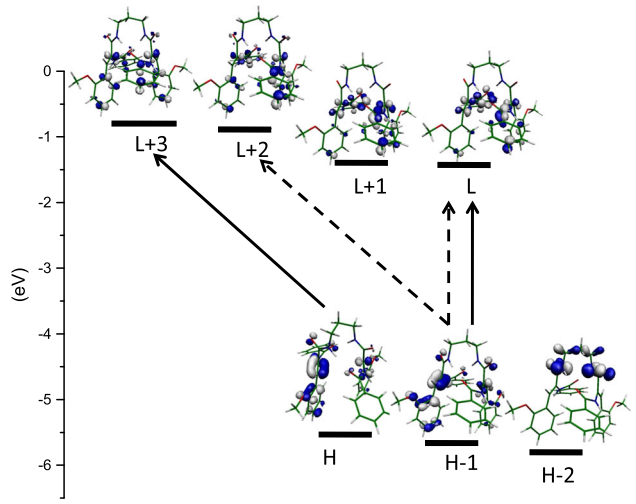


Figure 5. Representation of the molecular orbitals corresponding to the one-electron excitation involved in the transition calculated for S_3 and S_{10} in gas (solid line) and S_3 and S_{11} in the presence of solvent (dashed line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

4H, J = 7.2 Hz), 7.75 (d, 2H, J = 2.4 Hz), 7.45–7.58 (m, 6H), 7.37 (dd, 2H, ^1J = 8.6, ^2J = 2.4 Hz), 7.17 (s, 2H, Benzilic), 3.30 (s, CH_2—CH_2). ^{13}C NMR (400 MHz, DMSO-d_6), δ: 18.5, 56.0, 122.7, 127.3, 127.4, 127.7, 127.9, 128.2, 128.5, 128.9, 130.6, 131.2, 131.7, 132.0, 132.9, 133.2, 133.3, 134.0, 164.7, 165.8. $C_{34}H_{26}Cl_4N_4O_4$ Calcd: C, 58.64%; H, 3.76%; N, 8.05%; Found: C, 58.61%; H, 3.78%; N, 8.02%. UV–vis (λ_{max}, nm): 315.

N,N′-(1E,1′E)-3,3′-(Ethane-1,2-diylbis(azanediyl))bis(1-(4-bromophenyl)-3-oxoprop-1-ene-3,2-diyl)dibenzamide (2f). mp 133–135°C (decomp.); IR (KBr): ν (cm^{-1}): 3373, 3271, 3060, 2961, 22880, 1651, 1581, 1508, 1481, 1279, 1074, 1009, 710. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 10.02 (s, 2H, N—H Benzamide), 8.37 (s, 2H, N—H amide), 7.99 (d, 4H, J = 7.2 Hz), 7.45–7.59 (m, 10H), 7.14 (s, 2H, C=C alkene), 3.25 (s, 4H, CH_2—CH_2). ^{13}C NMR (100 MHz, DMSO-d_6), δ: 41.0, 121.5, 121.6, 126.9, 127.3, 127.4, 127.9, 128.2, 128.3, 129.0, 130.9, 131.1, 131.4, 131.7, 133.5, 133.6, 133.7, 165.2, 165.7, 173.0. $C_{34}H_{28}Br_2N_4O_4$ Calcd: C, 57.00%; H, 3.94%; N, 7.82%; Found: C, 57.02%; H, 3.95%; N, 7.80%. UV–vis (λ_{max}, nm): 312.

N,N′-(1E,1′E)-3,3′-(Ethane-1,2-diylbis(azanediyl))bis(1-(4-nitrophenyl)-3-oxoprop-1-ene-3,2-diyl)dibenzamide (2g). mp 152–155°C; IR (KBr): ν (cm^{-1}): 3445, 3332, 3230, 3068, 2928, 2875, 1646, 1597, 1509, 1478, 1342, 1281, 1110, 711. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 10.14 (s, 2H, N—H Benzamide), 8.47 (s, 2H, N—H amide), 8.19 (d, 4H, J = 8.8 Hz), 7.96 (d, 4H, J = 7.6 Hz), 7.75 (d, 4H, J = 8.8 Hz), 7.58 (t, 2H, J = 7.2 Hz), 7.48 (t, 4H, J = 7.6 Hz), 7.18 (s, 2H, Benzilic), 3.35 (s, 4H, CH_2—CH_2). ^{13}C NMR (100 MHz, DMSO-d_6), δ: 21.1, 123.6, 125.2, 128.0, 128.3, 130.0, 131.8, 133.3, 133.6, 141.5, 146.4, 165.0, 165.8, 172.0. $C_{34}H_{28}N_6O_8$ Calcd: C, 62.96%; H, 4.35%; N, 12.96%; Found: C, 62.98%; H, 4.38%; N, 12.93%. UV–vis (λ_{max}, nm): 335, 358.

N,N′-(1E,1′E)-3,3′-(Propane-1,3-diylbis(azanediyl))bis(3-oxo-1-(thiophen-2-yl)prop-1-ene-3,2- diyl)dibenzamide (3a). mp 160–164°C; IR (KBr): ν (cm^{-1}): 3349, 3250, 3067, 2925, 1650, 1621, 1526, 1466, 1271, 1282, 1210, 701, 642. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 9.83 (s, 2H, N—H Benzamide), 8.17 (t, 2H, J = 6.0 Hz, N—H amide), 8.09 (d, 4H, J = 7.2 Hz), 7.65 (s, 2H), 7.59–7.63 (m, 4H), 7.52–7.56 (t, 4H, J = 7.2 Hz), 7.41 (d, 2H, J = 3.2 Hz), 7.09 (dd, 2H, ^1J = 4.2, ^2J = 3.6 Hz), 3.37 (s, 4H, CH_2—N), 1.60 (m, 2H, C—CH_2—C). ^{13}C NMR (100 MHz, DMSO-d_6), δ: 29.4, 36.52, 125.2, 126.9, 127.0, 128.2, 128.3, 130.8, 131.7, 133.0, 133.9, 137.0, 164.9, 166.1. $C_{31}H_{28}N_4O_4S_2$ Calcd: C, 63.68%; H, 4.83%; N, 9.58%; S, 10.97%; Found: C, 63.66%; H, 4.81%; N, 9.60%, S, 10.93%. UV–vis (λ_{max}, nm): 325.

N,N′-(1E,1′E)-3,3′-(Propane-1,3-diylbis(azanediyl))bis(1-(2-methoxyphenyl)-3-oxoprop-1-ene-3,2-diyl)dibenzamide (3b). mp 113–115°C; IR (KBr): ν (cm^{-1}): 3408, 3314, 3253, 3067, 2935, 2840, 1649, 1578, 1517, 1479, 1252, 1020, 755, 711. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 9.84 (s, 2H, N—H Benzamide), 8.18 (t, J = 5.6 Hz, 2H, N—H amide), 7.96 (d, 2H, J = 7.2 Hz), 7.55 (t, 2H, J = 7.2 Hz), 7.47 (t, 6H, J = 7.6 Hz), 7.41 (s, 2H), 7.28 (td, 2H, ^1J = 8, ^2J = 1.6 Hz), 7.04 (d, 2H, J = 8.4 Hz), 6.84 (t, 2H, J = 7.2 Hz), 3.83 (s, 6H, O—CH_3), 3.22 (d, J = 6.0 Hz, 4H, CH_2—N), 1.63 (t, 2H, J = 6.4 Hz, C—CH_2—C). ^{13}C NMR (100 MHz, DMSO-d_6), δ: 29.3, 36.4, 55.5, 56.0, 111.1, 120.1, 122.9, 123.7, 127.4, 128.0, 128.1, 128.5, 130.0, 131.5, 138.0, 157.1, 165.0, 166.1. $C_{37}H_{36}N_4O_6$ Calcd: C, 70.24%; H, 5.74%; N, 8.86%; Found: C, 70.25%; H, 5.72%; N, 8.85%. UV–vis (λ_{max}, nm): 328.

N,N′-(1E,1′E)-3,3′-(Propane-1,3-diylbis(azanediyl))bis(1-(4-methoxyphenyl)-3-oxoprop-1-ene-3,2-diyl)dibenzamide (3c). mp 120–121°C (decomp.); IR (KBr): ν (cm^{-1}): 3360, 3278, 3067, 2935, 2837, 1649, 1602, 1577, 1512, 1477, 1253, 1176, 1029, 828, 704. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 9.92 (s, 2H, N—H Benzamide), 8.18 (t, 2H, J = 6.0 Hz, N—H amide), 8.03 (d, 4H, J = 7.6 Hz), 7.50–7.60 (m, 10H), 7.20 (s, 2H, Benzilic), 6.91 (d, 4H, J = 8.8 Hz), 3.74 (s, 6H, OCH_3), 3.21 (d, 4H, J = 6.0 Hz, CH_2—N), 1.57 (m, 2H, C—CH_2—C). ^{13}C NMR (100 MHz, DMSO-d_6), δ: 25.3, 37.0, 55.1, 114.0, 126.7, 126.8, 127.9, 128.0, 128.2, 128.3, 129.0, 131.0, 131.5, 133.8, 159.5, 159.5, 165.0, 165.2, 165.9. $C_{37}H_{36}N_4O_6$Calcd: C, 70.24%; H, 5.74%; N, 8.86%; Found: C, 70.25%; H, 5.72%; N, 8.86%. UV–vis (λ_{max}, nm): 318.

N,N′-(1E,1′E)-3,3′-(Propane-1,3-diylbis(azanediyl))bis(1-(4-chlorophenyl)-3-oxoprop-1-ene-3,2-diyl)dibenzamide (3d). mp 148–150°C (decomp.); IR (KBr): ν (cm^{-1}): 3422, 3278, 3064, 2938, 1654, 1579, 1521, 1478, 1284, 1093, 1013, 706. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 9.97 (s, 2H, N—H Benzamide), 8.25 (s, 2H), 7.98 (d, 4H, J = 6.8), 7.48–7.60 (m, 10H), 7.41 (d, 4H, J = 6.8 Hz), 7.14 (s, 2H, Benzilic), 3.22 (d, 4H, J = 5.6 Hz), 1.64 (m, 2H, C—CH_2—C). ^{13}C NMR (100 MHz, DMSO-d_6), δ: 29.1, 36.5, 127.1, 127.4, 127.9, 128.2, 128.3, 128.5, 130.1, 131.0, 131.7, 132.8, 133.3, 133.5, 164.9, 165.9. $C_{35}H_{30}Cl_2N_4O_4$ Calcd: C, 65.53%; H, 4.71%; N, 8.73%; Found: C, 65.54%; H, 4.69%; N, 8.70%. UV–vis (λ_{max}, nm): 320.

N,N′-(1E,1′E)-3,3′-(Propane-1,3-diylbis(azanediyl))bis(1-(2,4-dichlorophenyl)-3-oxoprop-1-ene-3,2-diyl)dibenzamide (3e). mp 76–78°C (decomp.); IR (KBr): ν (cm^{-1}): 3378, 3260, 2935.13, 2836.77, 1649.80, 1602.56, 1576.52, 1511.92, 1477.21, 1253.50, 1176.36, 1028.84, 703.89. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 9.93 (s, 2H, N—H Benzamide), 8.35 (t, 2H, J = 6.0 Hz, N—H amide), 7.91 (d, 4H, J = 7.2 Hz), 7.69 (d, 2H, J = 1.2 Hz), 7.45–7.58 (m, 10H), 7.37 (dd, 2H, ^1J = 8.6, ^2J = 2.4 Hz), 7.16 (s, 2H, Benzilic), 3.26 (s, 4H, H_2C—N), 1.67 (m, 2H, C—CH_2—C). ^{13}C NMR (100 MHz, DMSO-d_6), δ: 29.0, 36.6, 122.7, 126.0, 127.3, 127.4, 127.6, 127.7, 127.9, 128.2, 128.5, 128.9, 129.1, 129.9, 130.6,

131.0, 131.2, 131.7, 132.0, 133.1, 133.2, 133.4, 134.2, 164.4, 165.9. $C_{35}H_{28}Cl_4N_4O_4$ Calcd: C, 59.17%; H, 3.97%; N, 7.89%; Found: C, 59.19%; H, 3.95%; N, 7.88%. UV–vis (λ_{max}, nm): 317.

N,N′-(1E,1′E)-3,3′-(Propane-1,3-diylbis(azanediyl))bis(1-(4-bromophenyl)-3-oxoprop-1-ene-3,2-diyl)dibenzamide (3f). mp 154–156°C; IR (KBr): ν (cm^{-1}): 3422, 3276, 3062, 2936, 1654, 1581, 1519, 1472, 1274, 1074, 1009, 704. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 9.96 (s, 2H, N—H Benzamide), 8.25 (t, 2H, J = 6.0 Hz, N—H amide), 7.98 (d, 4H, J = 7.6 Hz), 7.46–7.60 (m, 14H), 7.11 (s, 2H, Benzilic), 3.22 (d, 4H, J = 6.4 Hz, CH_2—CH_2), 1.64 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6), δ: 29.0, 41.5, 119.6, 119.9, 121.6, 126.6, 127.7, 128.7, 130.3, 130.7, 131.7, 132.6, 133.6, 134.2, 135.1, 135.4, 164.9, 165.9, 167.8, 173.8. $C_{35}H_{30}Br_2N_4O_4$ Calcd: C, 57.55%; H, 4.14%; N, 7.67%; Found: C, 57.53%; H, 4.16%; N, 7.70%. UV–vis (λ_{max}, nm): 325.

N,N′-(1E,1′E)-3,3′-(Propane-1,3-diylbis(azanediyl))bis(1-(4-nitrophenyl)-3-oxoprop-1-ene-3,2-diyl)dibenzamide (3g). mp 237–239°C; IR (KBr): ν (cm^{-1}): 3438, 3414, 3234, 3066, 2937, 2871, 1653, 1598, 1518, 1474, 1343, 1278, 1110, 691. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 10.13 (s, 2H, N—H Benzamide), 8.38 (t, 2H, J = 5.6 Hz, N—H amide), 8.19 (d, 4H, J = 8.8 Hz), 7.97 (d, 4H, J = 7.2 Hz), 7.76 (d, 4H, J = 8.8 Hz), 7.57 (t, 2H, J = 7.6 Hz), 7.50 (t, 4H, J = 7.6 Hz), 7.17 (s, 2H, Benzilic), 2.88 (m, 4H), 1.68 (m, 2H, C—CH_2—C). ^{13}C NMR (100 MHz, DMSO-d_6), δ: 28.9, 36.5, 36.6, 123.5, 127.8, 128.0, 128.2, 130.0, 131.6, 141.8, 146.2, 164.9, 165.9. $C_{35}H_{30}N_6O_8$ Calcd: C, 63.44%; H, 4.56%; N, 12.68%; Found: C, 63.47%; H, 4.55%; N, 12.69%. UV–vis (λ_{max}, nm): 323.

N,N′-((1E,1′E)-(1,2-Phenylenebis(azanediyl))bis(1-(4-chlorophenyl)-3-oxoprop-1-ene-3,2-diyl))dibenzamide (4d). mp 138–140°C (decomp.); IR (KBr): ν (cm^{-1}): 3360, 3281, 3062, 2935, 2837, 1651, 1602, 1577, 1512, 1477, 1253, 1176, 1029, 828, 704. ^{1}H NMR (400 MHz, DMSO-d_6), δ: 9.92 (s, 2H, N—H Benzamide), 8.25 (d, 2H, J = 7.6 Hz), 8.18 (t, 2H, J = 6.0 Hz, N—H amide), 8.03 (d, 4H, J = 7.6 Hz), 7.50–7.60 (m, 10H), 7.20 (s, 2H, Benzilic), 7.07 (d, 2H, J = 7.5 Hz), 6.91 (d, 4H, J = 8.8 Hz), 3.74 (s, 6H, OCH_3), 3.21 (d, 4H, J = 6.0 Hz, CH_2—N), 1.57 (m, 2H, C—CH_2—C). ^{13}C NMR (100 MHz, DMSO-d_6), δ: 114.0, 124.5, 124.8, 126.7, 126.8, 127.9, 128.0, 128.2, 128.3, 129.0, 131.0, 131.5, 133.8, 159.5, 159.5, 165.0, 165.2, 165.9. $C_{38}H_{28}Cl_2N_4O_4$ Calcd: C, 67.56%; H, 4.18%; N, 8.29%; Found: C, 67.55%; H, 4.20%; N, 8.29%.

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