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ORIGINAL PAPER

Design and synthesis of new functionalized isoindigo and (3*Z*,3′*Z*)-3,3′-(ethane-1,2-diylidene)bis(indolin-2-one) derivatives

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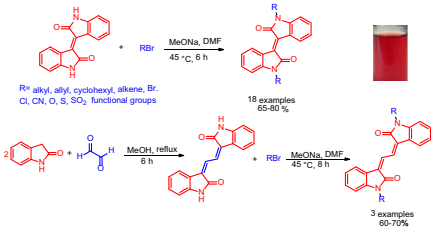
Abstract

A library of N,N-substituted isoindigo derivatives were prepared by reaction of isoindigo with a variety of alkylating agents in the presence of MeONa under mild conditions in yields of 65–80%. A new, more efficient synthesis of (3*Z*,3′*Z*)-3,3′-(ethane-1,2-diylidene)bis(indolin-2-one) is described by reaction of oxindole with glyoxal at reflux in methanol—a small library of N,N′-substituted derivatives were also prepared in 60–70% yield.

Graphical abstract



Keywords Isoindigo · Oxindole · (3*Z*,3′*Z*)-3,3′-(Ethane-1,2-diylidene)bis(indolin-2-one)

Introduction

Organic π-conjugated compounds are increasingly important as promising candidates in conductance, photonics, and magnetism due to their π-electronic communication. In particular, organic π-conjugated small molecules have been studied extensively because of their unique applications in optical and electronic materials [1, 2]. In this area, organic semiconductors are finding widespread use as replacements for their inorganic counterparts to develop their potential applications in flexible and low-cost organic opto-electronic devices, such as organic field-effect transistors (OFETs) [3–5], organic photovoltaic (OPVs) [6–8], and organic light-emitting devices (OLEDs) [9, 10]. A successful method to prepare of π-conjugated organic materials entails the creation of donor–acceptor (D–A) units, having both electron-donating and electron-withdrawing structures [11]. In this approach, a π-electron rich donor is combined with a π-electron-deficient acceptor, with the interaction of their frontier orbitals, reducing the effective bandgap [12]. Among them, perylene imides [13], bithiophene imides [14], naphthalenediimides [15], and diketopyrroles [11, 16] have been extensively studied as polymeric donors and building blocks for donor–acceptor type molecular architecture in recent years. One amide/imide acceptor employed to date is isoindigo which has attracted considerable attention as a useful building block

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to construct high-performance organic semiconductors [17–19]. The two fused, planar lactam rings adjacent to the aryl moieties endow the unit with a strong electron-withdrawing nature and represent a highly reactive conjugated system. This allows these molecules to be incorporated into materials for transistor applications due to their extended delocalised planar aromatic π-system, which may facilitate π–π stacking and enable high-charge carrier mobility [20]. Copolymers based on these nitrogen-containing electron-deficient dyes have been developed for organic solar cells [21].

Results and discussion

In general, *N*-alkyl isoindigo compounds are prepared by the reaction of alkyl halides with isoindigo in the presence of potassium carbonate under thermal conditions (100 °C) [22]. In addition, the reaction of haloalkyl isatins with tris(diethylamino)phosphine at low temperature (− 60 °C) forms isoindigo compounds with two haloalkyl functional groups [23–25]. Due to the widespread applications of substituted isoindigos, we investigated the breadth of N,N′-disubstituted analogs, with subsequent reactions to extend the catalog of possible derivatives—this included an array of chains or rings bearing bromo, chloro, nitrile, benzyl ether, allyl, alkene, cyclohexene, and cyclohexane. Further, we applied this strategy to the reaction with the π-extended conjugated compound, (3*Z*,3′*Z*)-3,3′-(ethane-1,2-diylidene)bis(indolin-2-one).

Therefore, to a stirred solution of isoindigo **1** sodium methoxide was added followed by the alkyl bromide, and after stirring at 45 °C for 6 h, and upon workup, the N,N′-disubstituted isoindigos were isolated in 65–80% yield (Scheme 1).

In a typical example, analysis of the ^{13}C NMR spectra of compound **2m** showed a resonance at δ = 166.9 ppm assigned to the carbonyl group, confirming the molecular symmetry. Analysis of the ^{1}H NMR spectrum showed a doublet at 9.16 ppm with J = 8.0 Hz assigned to H4. For this compound, broad absorption bands with two maxima at 280 and 390 nm were observed in the UV–Vis spectrum. The structure of **2m** was unambiguously confirmed by X-ray crystallographic analysis (Fig. 1).

The substrate scope of substituted isoindigos was then further explored through the reaction of (*E*)-1,1′-bis(5-bromopentyl)-[3,3′-biindolinylidene]-2,2′-dione (**2e**) with thios. The reaction of **2e** with sodium thiophenolate (**3**) in DMF at 70 °C for 6 h gave (*E*)-1,1′-bis[5-(phenylthio)-pentyl]-[3,3′-biindolinylidene]-2,2′-dione (**4a**) in 65% yield (Scheme 2). Analysis of the ^{1}H NMR spectrum showed resonances at 7.45, 7.52, and 7.78 ppm assigned to the thiophenyl protons, whereas the ^{13}C NMR spectrum showed a resonance at 55.9 ppm assigned to the CH_2S group.

The utility of the protocol was extended to the reaction of **2e** with 2-mercaptobenzothiazole (**5**) in CH_2Cl_2 at reflux to give the (*E*)-1,1′-bis[5-(benzo[*d*]thiazol-2-ylthio)-pentyl]-[3,3′-biindolinylidene]-2,2′-dione (**6a**) in satisfactory yield (Scheme 3). Analysis of the FT-IR spectrum of **6a** showed absorption at 1690 cm^{-1} assigned to the carbonyl moiety.

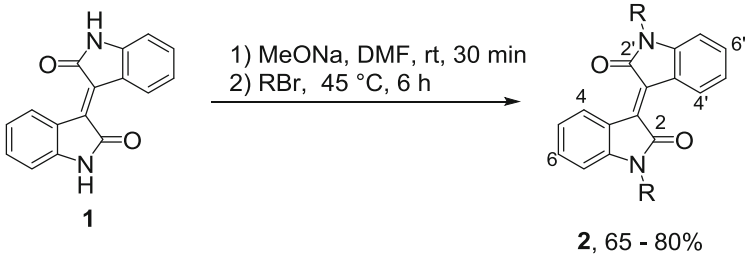
Molecules that contain a pyrimidine nucleus possess a wide range of biological activities and occur in living systems in the form of vitamins and nucleic acids [26–28] and, therefore, compound **8a** (Scheme 4) was synthesised by reaction of **2e** with 2-mercaptopyrimidine (**7**) in the presence of trimethylamine at 80 °C for 4 h. Analysis of the ^{1}H NMR spectrum revealed a triplet at 6.93 ppm (J = 8.0 Hz) and a doublet at 8.47 ppm (J = 8.0 Hz), assigned to the pyrimidyl H5′ and H4′/6′ protons, respectively, whereas the ^{13}C NMR spectrum displayed the characteristic resonance at 166.8 ppm assigned to the isoindigo carbonyl, and a resonance at 156.1 ppm assigned to the pyrimidyl C2′. The HR-ESI mass spectrum showed a peak at *m*/z = 617.1768, assigned to the molecular formula $C_{32}H_{30}N_6O_2S_2$ and was indicative of the addition of two thiopyrimidine unit.

Sulfones can also possess interesting biological activity [29, 30] and, therefore, (*E*)-1,1′-bis(5-bromopentyl)-[3,3′-biindolinylidene]-2,2′-dione (**2e**) was reacted with sodium benzenesulfinate producing (*E*)-1,1′-bis[5-(phenylsulfonyl)pentyl]-[3,3′-biindolinylidene]-2,2′-dione (**10a**), incorporating the sulfonyl functional group (Scheme 5).

The isoindigo analog (3*Z*,3′*Z*)-3,3′-(ethane-1,2-diylidene)bis(indolin-2-one) (**12**) is an extended π-conjugate dimeric heterocycle in which two oxindole rings are connected by an ethylene. This structure is less rigid than isoindigo due rotational freedom in the single bonds. Its synthesis is reported as a two-step process (22 and 74% yield, 16% overall) [31] and its application as an attractive building block for conjugated photovoltaic polymers has been recently reported [32]. Therefore, we extended our isoindigo alkylation strategy to include the π-extended heterocycles **12**. The synthesis of the parent structure was achieved by heating oxindole **11** with glyoxal in methanol at reflux producing **12** in 32% yield in a single step (Scheme 6).

Utilizing the same alkylation strategy, (3*Z*,3′*Z*)-3,3′-(ethane-1,2-diylidene)bis(indolin-2-one) **4** was reacted with a variety of alkyl halides to produce **13a**–**13c** in yields of 60–70% (Scheme 7). Analysis of the ^{1}H NMR spectra of (3*Z*,3′*Z*)-3,3′-(ethane-1,2-diylidene)bis(1-isopropylindolin-2-one) (**5a**) showed a sharp singlet at 8.98 ppm, assigned to the two central olefinic protons in an *s-trans* configuration. Analysis of the FT-IR spectrum of **13a** showed absorption

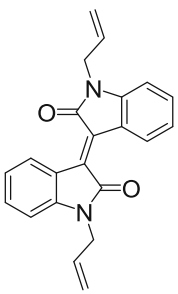
Scheme 1



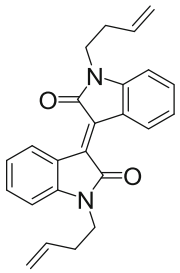
1

2, 65 - 80%

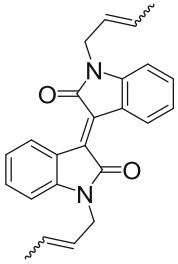
products structure



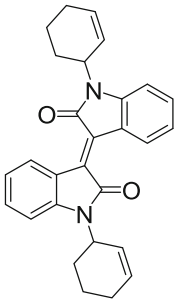
2a,80%



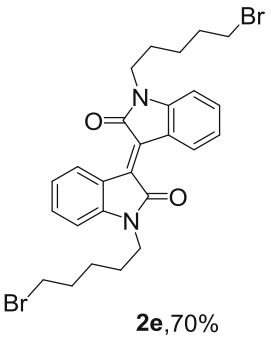
2b,71%



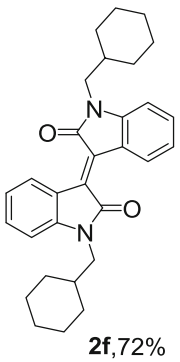
2c,67%(*E*/*Z*, 63/37)



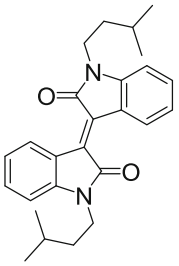
2d,68%



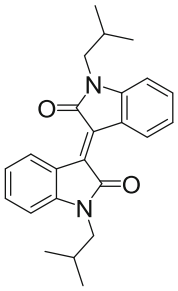
2e,70%



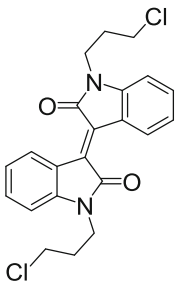
2f,72%



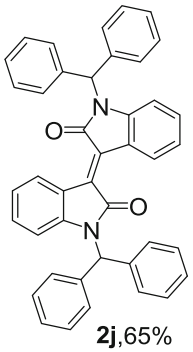
2g,69%



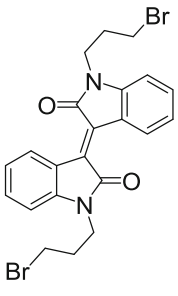
2h,65%



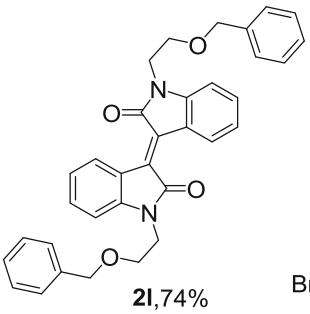
2i,72%



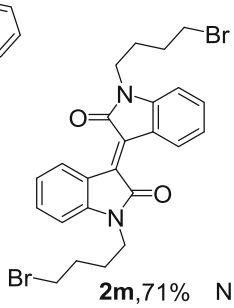
2j,65%



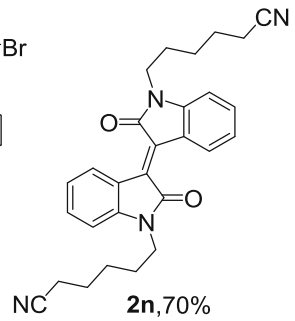
2k,68%



2l,74%



2m,71%



2n,70%

at 1689 cm^{-1} assigned to the two carbonyl moieties and analysis of the UV–Vis spectrum showed two maximum absorptions at 228 and 386 nm for this red compound.

Conclusion

In summary, we have developed an efficient, high yielding, and attractive alkylation of isoindigo and its π-extended analog **12** with a range of alkylating agents using MeONa

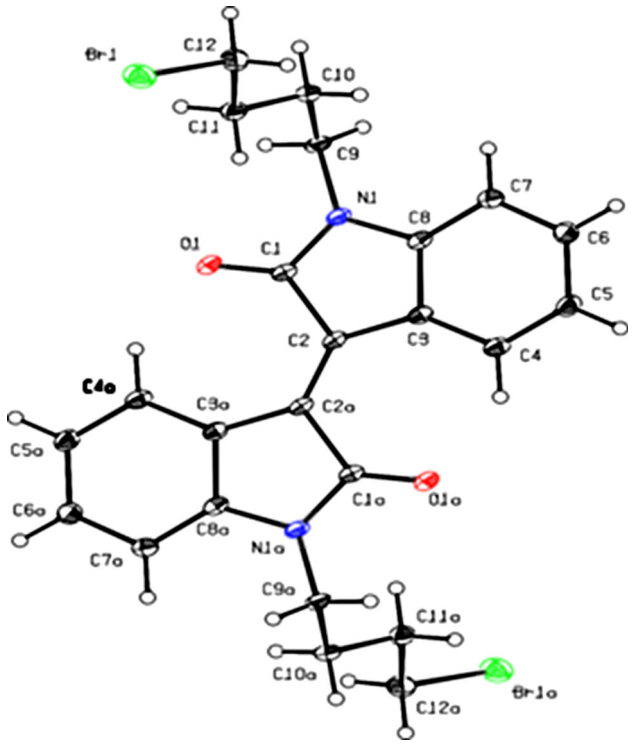


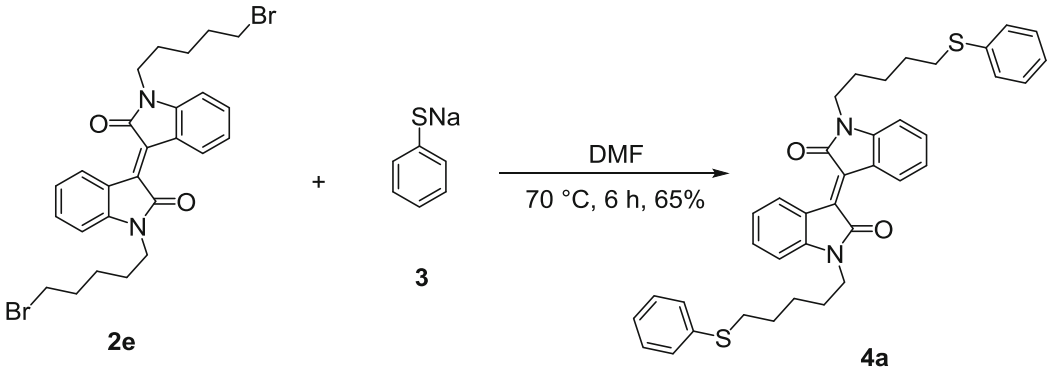
Fig. 1 The X-ray crystal structure **2m**

as the base under mild conditions. Previous alkylation strategies for isoindigo relied on DMF solutions using K_2CO_3 and heating to 100 °C for up to 24 h—while these could produce reasonable yields [18], our milder conditions with shorter reaction represents an improved strategy. The products are highly functionalized molecules, potentially amenable to further manipulations. Notably, the preparation of analog (3*Z*,3′*Z*)-3,3′-(ethane-1,2-diylidene)bis(indolin-2-one) (**12**) in 32% yield as a π-extended conjugated compound by condensation of oxindole with glyoxal compound represents a more efficient single step, higher yielding methodology using inexpensive reagents compared to that previously published. We are currently using this new method for the construction of new isoindigo derivatives with potential electronic, biological, and pharmaceutical activities.

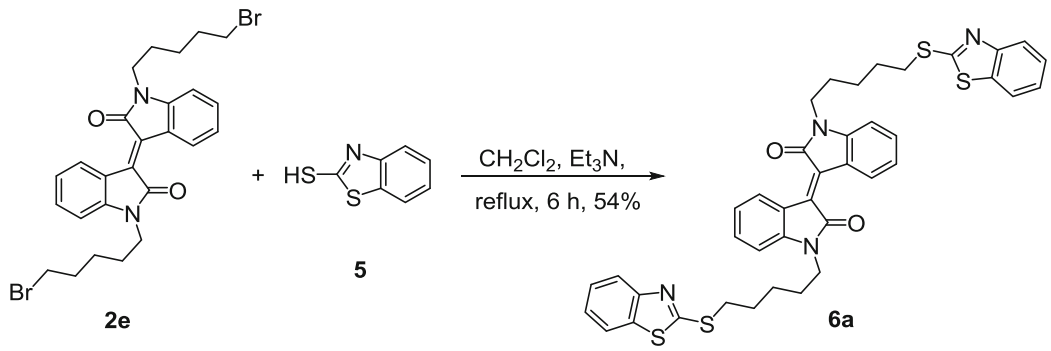
Experimental

Reagents and solvents were purchased reagent grade and used without further purification except isoindigo [33]. All reactions were performed in standard oven-dried glassware

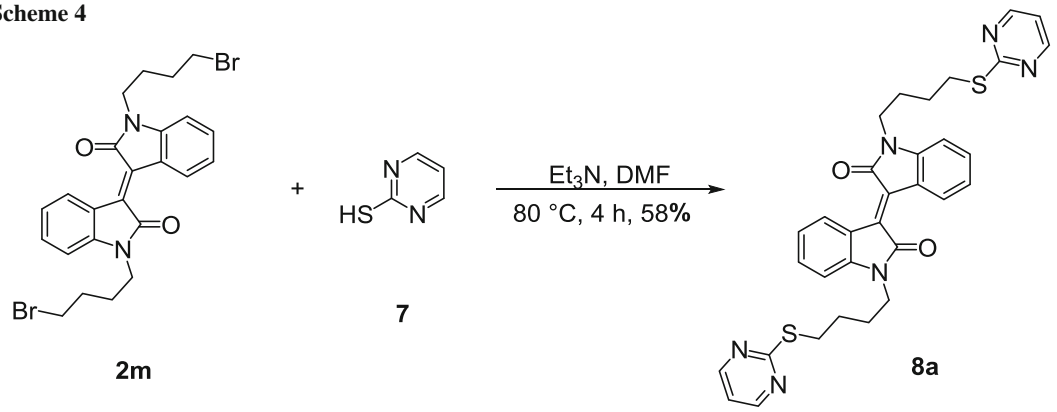
Scheme 2



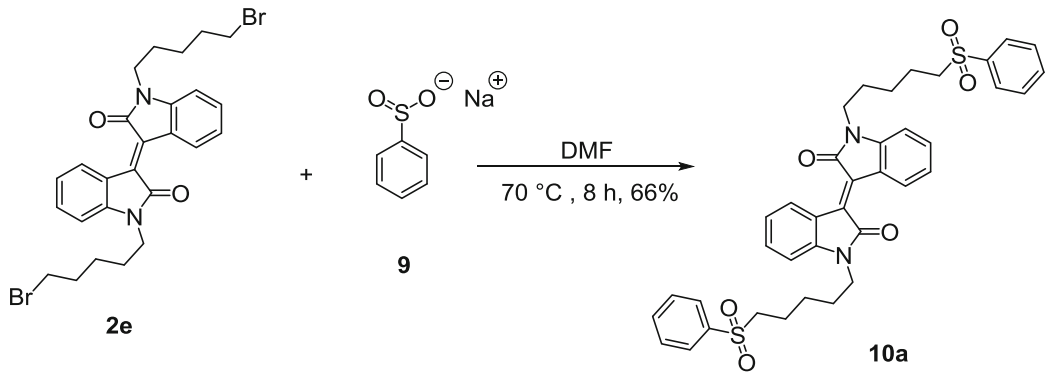
Scheme 3



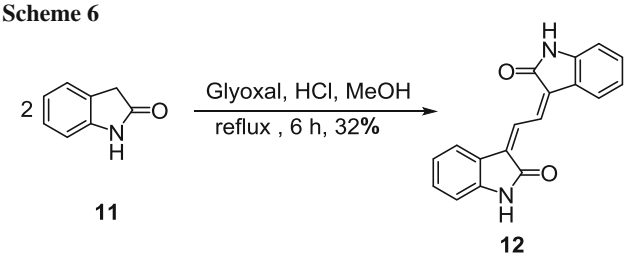
Scheme 4



Scheme 5



Scheme 6

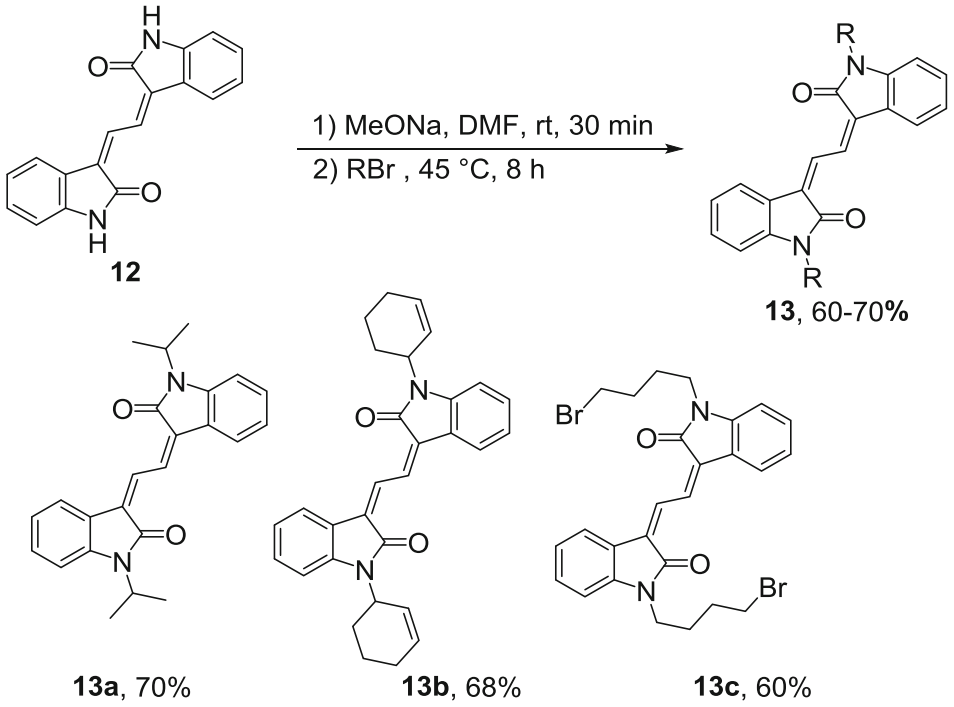


under a nitrogen atmosphere unless otherwise stated. ^{1}H and ^{13}C NMR spectra ($CDCl_3$ solutions) were recorded at 400 and 100.6 MHz with chemical shifts (δ) reported in parts per million relative to TMS (δ = 0 ppm) or $CDCl_3$ (δ = 77.0 ppm) as internal standards. Coupling constants (*J*) are reported in Hertz (Hz). Multiplicities are reported as singlet (s), broad singlet (bs), doublet of doublets (dd), or multiplet (m). High-resolution electrospray (HR-ESI—single quadrupole) mass spectra have their ion mass to charge (*m/z*) values stated with their relative abundances as a percentage in parentheses. Peaks assigned to the molecular ion are denoted by $[M+H]^+$ or $[M+Na]^+$. Infrared (IR) spectra were recorded on neat samples. UV–Vis spectra were recorded with solutions of samples in CH_2Cl_2. Thin-layer chromatography (TLC) was performed using Silica Gel F254 aluminum sheets. Column chromatography was performed under gravity using Silica Gel 60 (0.063–0.200 mm). Eluents are in volume to volume (*v*:*v*) proportions. Solvent extracts or chromatographic fractions were concentrated by rotary evaporation in vacuo.

General procedure for the preparation of 2

To a magnetically stirred solution of 131 mg isoindigo **1** (0.5 mmol) in 3 cm^3 DMF, 59.4 mg sodium methoxide solution (1.1 mmol) was added in 2 cm^3 DMF at room temperature. The reaction mixture stirred for 30 min, followed by the addition of the alkyl bromide (3 mmol) and the reaction stirred for 6 h at 45 °C. The mixture was poured into 10 cm^3 H_2O, extracted with 20 cm^3 CH_2Cl_2, dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was subjected to silica gel column chromatography using hexane–ethyl acetate as eluent.

Scheme 7



(*E*)-1,1′-Diallyl-[3,3′-biindolinylidene]-2,2′-dione (2a) Dark red powder; yield 80%; m.p.: 166 °C. Spectroscopic data are in agreement with that reported [25].

(*E*)-1,1′-Dibut-3-en-1-yl-[3,3′-biindolinylidene]-2,2′-dione (2b, $C_{24}H_{22}N_2O_2$) Dark red powder; yield 78%; m.p.: 98 °C; IR (KBr): $\bar{\nu}$ = 1683, 1606, 1080, 669, 557 cm^{-1}; $\lambda_{max/nm}$ (ε) = 258 (4000), 374 (3850) nm (M^{-1} cm^{-1}); ^1H NMR (400.1 MHz, $CDCl_3$): δ = 2.46 (td, J = 10.2, 1.1 Hz, 4H), 3.82–3.86 (m, 4H), 5.04–5.13 (m, 4H), 5.79–5.89 (m, 2H), 6.79 (dd, J = 7.8, 0.4 Hz, 2H), 7.04 (td, J = 7.7 1.0 Hz, 2H), 7.35 (td, J = 7.7, 1.2 Hz, 2H), 9.18 (dd, J = 8.0, 0.7 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 31.8, 39.4, 107.8, 117.5, 121.7, 122.2, 129.9, 132.3, 133.4, 134.4, 144.4, 167.8 ppm; HRMS (ESI): $[M+H]^+$ calcd for $C_{24}H_{23}N_2O_2$ 371.1760, found 371.1754.

(*E*)-1,1′-(*E*/*Z*)-Dibut-2-en-1-yl-[3,3′-biindolinylidene]-2,2′-dione (2c, $C_{24}H_{22}N_2O_2$) Dark red powder; yield 76%; m.p.: 128 °C; IR (KBr): $\bar{\nu}$ = 1683, 1606, 1433, 1378, 1103, 776 cm^{-1}; $\lambda_{max/nm}$ (ε) = 263 (4000), 363 (3791) nm (M^{-1} cm^{-1}); ^1H NMR (400.1 MHz, $CDCl_3$): (*E*) δ = 1.67–1.69 (m, 6H), 4.33–4.35 (m, 4H), 5.41–5.52 (m, 2H), 5.71–5.76 (m, 2H), 6.73–6.79 (m, 2H), 7.04 (td, J = 7.9, 1.1 Hz, 2H), 7.32 (td, J = 7.6, 1.1 Hz, 2H), 9.20 (dd, J = 8.0, 0.4 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.6, 41.6, 108.3, 122.2, 123.9, 129.1, 129.9, 130.0, 132.2, 133.4, 144.6, 167.5 ppm; ^1H NMR (400.1 MHz, $CDCl_3$): (*Z*) δ = 1.84–1.86 (m, 6H), 4.45 (dd, J = 6.4, 0.4 Hz, 4H), 5.41–5.52 (m, 2H), 5.71–5.76 (m, 2H), 6.73–6.79 (m, 2H), 7.04 (td, J = 7.9, 1.1 Hz, 2H), 7.32 (td, J = 7.6,1.1 Hz, 2H), 9.20 (dd, J = 8.0, 0.4 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.2, 36.9, 108.1, 121.6, 123.9, 124.1, 128.4, 129.8, 132.2, 133.4, 144.6, 167.5 ppm; HRMS (ESI): $[M+H]^+$ calcd for $C_{24}H_{23}N_2O_2$ 371.1760, found 371.1774.

(*E*)-1,1′-Dicyclohex-2-en-1-yl-[3,3′-biindolinylidene]-2,2′-dione (2d, $C_{28}H_{26}N_2O_2$) Dark red powder; yield 68%; m.p.: 181 °C; IR (KBr): $\bar{\nu}$ = 1689, 1603, 1465, 1108, 725, 681 cm^{-1}; $\lambda_{max/nm}$ (ε) = 238 (4000), 403 (3940) nm (M^{-1} cm^{-1}); ^1H NMR (400.1 MHz, $CDCl_3$): δ = 1.78–1.85 (m, 2H), 1.92–1.98 (m, 6H), 2.01–2.18 (m, 4H), 5.25–5.27 (m, 2H), 5.67 (d, J = 10.1 Hz, 2H), 6.00–6.03 (m, 2H), 6.98–7.05 (m, 4H), 7.24–7.28 (m, 2H), 9.13 (dd, J = 7.9, 0.7 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.8, 24.5, 25.8, 48.5, 110.3, 121.8, 121.9, 127.6, 129.7, 131.0, 132.0, 133.4, 134.8, 167.6 ppm; HRMS (ESI): $[M+Na]^+$ calcd for $C_{28}H_{26}N_2O_2Na$ 445.1892, found 445.1904.

(*E*)-1,1′-Bis(5-bromopentyl)-[3,3′-biindolinylidene]-2,2′-dione (2e) Dark red powder; yield 76%; m.p.: 138 °C. Spectroscopic data are in agreement with that reported [23].

(*E*)-1,1′-Bis(cyclohexylmethyl)-[3,3′-biindolinylidene]-2,2′-dione (2f, $C_{30}H_{34}N_2O_2$) Dark red powder; yield 76%; m.p.:

145 °C; IR (KBr): $\bar{\nu}$ = 1687, 1607, 1460, 1448, 1355, 1087, 773 cm^{-1}; $\lambda_{max/nm}$ (ε) = 276 (3952), 391 (3263) nm (M^{-1} cm^{-1}); ^1H NMR (400.1 MHz, $CDCl_3$): δ = 1.04–1.22 (m, 10H), 1.65–1.75 (m, 10H), 1.80–1.85 (m, 2H), 3.60 (d, *J* = 7.3 Hz, 4H), 6.77 (d, *J* = 7.6 Hz, 2H), 7.03 (td, *J* = 7.7, 1.0 Hz, 2H), 7.33 (td, *J* = 7.7, 1.1 Hz, 2H), 9.15 (dd, *J* = 8.0, 0.7 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 25.7, 26.2, 31.1, 36.5, 46.4, 108.2, 121.6, 122.1, 129.8, 132.2, 133.5, 145.2, 168.2 ppm; HRMS (ESI): $[M+H]^+$ calcd for $C_{30}H_{35}N_2O_2$ 455.2699, found 455.2691.

(*E*)-1,1′-Diisopentyl-[3,3′-biindolinylidene]-2,2′-dione (2 g, $C_{26}H_{30}N_2O_4$) Dark red powder; yield 69%; m.p.: 106 °C; IR (KBr): $\bar{\nu}$ = 1683, 1608, 1356, 1098, 764 cm^{-1}; $\lambda_{max/nm}$ (ε) = 229 (1344), 277 (1505) nm (M^{-1} cm^{-1}); ^1H NMR (400.1 MHz, $CDCl_3$): δ = 0.99 (d, *J* = 6.5 Hz, 12H), 1.55–1.61 (m, 4H), 1.64–1.74 (m, 2H), 3.78 (t, *J* = 5.8 Hz,, 4H), 6.77 (d, *J* = 7.4 Hz, 2H), 7.03 (td, *J* = 7.7, 1.0 Hz, 2H), 7.33 (td, *J* = 7.6, 1.1 Hz, 2H), 9.18 (dd, *J* = 8.0, 0.7 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.5, 26.1, 36.0, 38.4, 107.7, 121.7, 122.1, 129.9, 132.2, 133.5, 144.6, 167.7 ppm; HRMS (ESI): $[M+H]^+$ calcd for $C_{26}H_{31}N_2O_4$ 403.2386, found 403.2388.

(*E*)-1,1′-Diisobutyl-[3,3′-biindolinylidene]-2,2′-dione (2 h, $C_{24}H_{26}N_2O_2$) Dark red powder; yield 74%; m.p.: 138 °C; IR (KBr): $\bar{\nu}$ = 1690, 1608, 1465, 1356, 1331, 1095, 775, 743 cm^{-1}; $\lambda_{max/nm}$ (ε) = 247 (4000), 361 (2626) nm (M^{-1} cm^{-1}); ^1H NMR (400.1 MHz, $CDCl_3$): δ = 0.99 (d, *J* = 6.6 Hz, 12H), 2.13–2.23 (m, 2H), 3.59 (d, *J* = 7.5 Hz, 4H), 6.78 (d, *J* = 7.8 Hz, 2H), 7.03 (td, *J* = 7.8, 1.0 Hz, 2H), 7.33 (td, *J* = 7.7, 1.1 Hz, 2H), 9.16 (dd, *J* = 8.0, 0.7 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.3, 27.2, 47.5, 108.1, 121.6, 122.1, 129.8, 132.2, 133.5, 145.1, 168.2 ppm; HRMS (ESI): $[M+H]^+$ calcd for $C_{24}H_{27}N_2O_2$ 375.2090, found 375.2073.

(*E*)-1,1′-Bis(3-chloropropyl)-[3,3′-biindolinylidene]-2,2′-dione (2i) Dark red powder; yield 76%; m.p.: 148 °C. Spectroscopic data are in agreement with that reported [24].

(*E*)-1,1′-Dibenzhydryl-[3,3′-biindolinylidene]-2,2′-dione (2j, $C_{42}H_{30}N_2O_2$) Dark red powder; yield 65%; m.p.: 293 °C; IR (KBr): $\bar{\nu}$ = 1690, 1604, 1477, 1453, 1005, 762, 749, 663 cm^{-1}; $\lambda_{max/nm}$ (ε) = 274 (3736), 402 (2059) nm (M^{-1} cm^{-1}); ^1H NMR (400.1 MHz, $CDCl_3$): δ = 6.40 (d, *J* = 7.9 Hz, 2H), 6.95 (td, *J* = 8.0, 1.0 Hz, 2H), 7.04 (td, *J* = 7.8, 1.2 Hz, 2H), 7.16 (s, 2H), 7.33 (br, 20H), 9.11 (dd, *J* = 7.9, 0.8 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 57.3, 110.5, 120.8, 121.0, 126.7, 127.4, 127.6, 128.6, 130.9, 132.3, 136.5, 143.0, 167.0 ppm; HRMS (ESI): $[M+H]^+$ calcd for $C_{42}H_{31}N_2O_2$ 595.2386, found 595.2403.

(*E*)-1,1′-Bis(3-bromopropyl)-[3,3′-biindolinylidene]-2,2′-dione (2 k) Dark red powder; yield 77%; m.p.: 178 °C. Spectroscopic data are in agreement with that reported [23].

(*E*)-1,1′-Bis[2-(benzyloxy)ethyl]-[3,3′-biindolinylidene]-2,2′-dione (2 l, $C_{34}H_{30}N_2O_4$) Dark red powder; yield 86%; m.p.: 130 °C; IR (KBr): $\bar{\nu}$ = 1683, 1604, 1465, 1347, 1031, 772, 696, 442 cm^{-1}; $\lambda_{max/nm}$ (ε) = 268 (4000), 394 (3089) nm (M^{-1} cm^{-1}); ^1H NMR (400.1 MHz, $CDCl_3$): δ = 3.75 (t, *J* = 5.7 Hz, 4H), 4.00 (t, *J* = 5.7 Hz, 4H), 4.51 (s, 4H), 6.90 (d, *J* = 7.6 Hz, 2H), 7.03 (td, *J* = 7.7, 1.0 Hz, 2H), 7.21–7.27 (m, 10H), 7.29–7.31 (m, 2H), 9.15 (dd, *J* = 8.0, 0.7 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 40.2, 67.4, 73.2, 108.6, 121.6, 122.2, 127.5, 127.6, 128.3, 129.7, 132.3, 133.3, 137.8, 144.9, 168.0 ppm; HRMS (ESI): $[M+Na]^+$ calcd for $C_{34}H_{30}N_2O_4Na$ 553.2103, found 553.2088.

(*E*)-1,1′-Bis(4-bromobutyl)-[3,3′-biindolinylidene]-2,2′-dione (2m, $C_{24}H_{24}Br_2N_2O_2$) Dark red powder; yield 71%; m.p.: 93 °C; IR (KBr): $\bar{\nu}$ = 1683, 1606, 1465, 1449, 1356, 773, 747 cm^{-1}; $\lambda_{max/nm}$ (ε) = 280 (3975), 390 (3706) nm (M^{-1} cm^{-1}); ^1H NMR (400.1 MHz, $CDCl_3$): δ = 1.87–1.98 (m, 8H), 3.46 (t, *J* = 6.3 Hz, 4H), 3.83 (t, *J* = 6.6 Hz, 4H), 6.81 (d, *J* = 7.7 Hz, 2H), 7.06 (td, *J* = 7.8, 1.0 Hz, 2H), 7.37 (td, *J* = 7.7, 1.2 Hz, 2H), 9.16 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 25.0, 28.7, 32.0, 37.9, 106.8, 120.6, 121.3, 128.9, 131.5, 132.4, 143.3, 166.9 ppm; HRMS (ESI): $[M+Na]^+$ calcd for $C_{24}H_{24}^{79}Br_2N_2O_2Na$ 553.0102, found 553.0115.

(*E*)-6,6′-(2,2′-Dioxo-[3,3′-biindolinylidene]-1,1′-diyl)dihexanenitrile (2n, $C_{28}H_{28}N_4O_2$) Dark red powder; yield 78%; m.p.: 105 °C; IR (KBr): $\bar{\nu}$ = 1680, 1608, 1468, 1455, 1350, 1161, 1095, 759, 774, 671 cm^{-1}; $\lambda_{max/nm}$ (ε) = 267 (3960), 392 (2638) nm (M^{-1} cm^{-1}); ^1H NMR (400.1 MHz, $CDCl_3$): δ = 1.52–1.58 (m, 4H), 1.67–1.77 (m, 8H), 2.34 (t, *J* = 7.1 Hz, 4H), 3.79 (t, *J* = 7.1 Hz, 4H), 6.77 (d, *J* = 7.4 Hz, 2H), 7.05 (td, *J* = 7.7, 1.0 Hz, 2H), 7.35 (td, *J* = 7.7, 1.1 Hz, 2H), 9.15 (dd, *J* = 8.0, 0.7 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.0, 25.0, 26.0, 26.7, 39.5, 107.7, 119.5, 121.6, 122.3, 129.9, 132.5, 133.4, 144.4, 167.8 ppm; HRMS (ESI): $[M+Na]^+$ calcd for $C_{28}H_{28}N_4O_2Na$ 475.2110, found 475.2105.

(*E*)-1,1′-Bis(5-phenylthio)-[3,3′-biindolinylidene]-2,2′-dione (4a, $C_{38}H_{38}N_2O_2S_2$) A mixture of 168 mg (*E*)-1,1′-bis(5-bromopentyl)-[3,3′-biindolinylidene]-2,2′-dione (**2e**, 0.3 mmol) and 132 mg sodium thiophenolate (**3**, 1 mmol) in 5 cm^3 DMF was stirred for 6 h at 70 °C. The resulting mixture was extracted with CH_2Cl_2 (2 × 10 cm^3), washed with 10 cm^3 water and the combined organic layers dried ($MgSO_4$) and concentrated. The residue was subjected to flash column chromatography (silica gel) using petroleum

ether–ethyl acetate (4:1) as eluent to give the dione. Dark red powder; yield 65%; m.p.: 142 °C; IR (KBr): $\bar{\nu}$ = 1690, 1604, 1477, 1465, 1453, 1423, 1005, 745 cm^{-1}; $\lambda_{max/nm}$ (ε) = 267 (3963), 395 (3883) nm (M^{-1} cm^{-1}); ^1H NMR (400.1 MHz, $CDCl_3$): δ = 1.34–1.38 (m, 4H), 1.58–1.61 (m, 4H), 1.65–1.69 (m, 4H), 2.98 (t, J = 7.8 Hz, 4H), 3.64 (t, J = 7.1 Hz, 4H), 6.64 (d, J = 7.7 Hz, 2H), 6.94 (td, J = 8.0, 0.7 Hz, 2H), 7.24 (td, J = 7.6, 1.0 Hz, 2H), 7.45 (t, J = 7.2 Hz, 4H), 7.52 (t, J = 7.1 Hz, 2H), 7.78 (t, J = 7.2 Hz, 4H), 9.02 (d, J = 7.9 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.4, 25.6, 27.0, 39.5, 55.9, 107.7, 121.5, 122.3, 127.9, 129.3, 129.9, 132.4, 133.3, 133.7, 139.0, 144.3, 167.8 ppm; HRMS (ESI): $[M+Na]^+$ calcd for $C_{38}H_{38}N_2O_2S_2Na$ 641.2273, found 641.2798.

(*E*)-1,1′-Bis[5-(benzo[d]thiazol-2-ylthio)pentyl]-[3,3′-biindolinylidene]-2,2′-dione (6a, $C_{40}H_{36}N_4O_2S_4$) A mixture of 168 mg (*E*)-1,1′-bis(5-bromopentyl)-[3,3′-biindolinylidene]-2,2′-dione (**2e**, 0.3 mmol), 167 mg 2-mercaptobenzothiazole (**5**, 1 mmol) and 101 mg triethylamine (1 mmol) in 6 cm^3 CH_2Cl_2 was heated at reflux with stirring for 6 h. The solvent was removed under reduced pressure and the residue subjected to silica gel column chromatography using petroleum spirit–ethyl acetate (4:1) as eluent to give the dione **6a**. Dark red powder; yield 54%; m.p.: 109 °C; IR (KBr): $\bar{\nu}$ = 1690, 1605, 1465, 1453, 1423, 1355, 1005, 749, 734 cm^{-1}; $\lambda_{max/nm}$ (ε) = 271 (3933), 301 (2942) nm (M^{-1} cm^{-1}); ^1H NMR (400.1 MHz, $CDCl_3$): δ = 1.49–1.55 (m, 4H), 1.66–1.74 (m, 4H), 1.78–1.85 (m, 4H), 3.25 (t, J = 7.3 Hz, 4H), 3.72 (t, J = 7.2 Hz, 4H), 6.70 (d, J = 7.7 Hz, 2H), 6.95 (td, J = 8.1, 0.9 Hz, 2H), 7.17–7.20 (m, 2H), 7.24 (td, J = 7.7, 1.0 Hz, 2H), 7.30 (td, J = 7.2, 1.1 Hz, 2H), 7.64 (d, J = 7.8 Hz, 2H), 7.76 (d, J = 8.1 Hz, 2H), 9.10 (d, J = 8.0 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 25.1, 26.0, 28.0, 32.2, 38.7, 106.8, 119.8, 120.4, 120.6, 121.2, 123.1, 124.9, 128.9, 131.3, 132.4, 134.1, 143.5, 152.2, 165.9, 166.8 ppm; HRMS (ESI): $[M+H]^+$ calcd for $C_{40}H_{37}N_4O_2S_4$ 733.1799, found 733.1830.

(*E*)-1,1′-Bis[4-(pyrimidin-2-ylthio)butyl]-[3,3′-biindolinylidene]-2,2′-dione (8a, $C_{32}H_{30}N_6O_2S_2$) A mixture of 159 mg (*E*)-1,1′-bis(4-bromobutyl)-[3,3′-biindolinylidene]-2,2′-dione (**2m**, 0.3 mmol), 112 mg 2-mercaptopyrimidine (**7**, 1 mmol) and 101 mg Et_3N (1 mmol) in 5 cm^3 DMF was stirred for 6 h at 80 °C. The resulting mixture was extracted with CH_2Cl_2 (2 × 10 cm^3), washed with 10 cm^3 water and the combined organic layers dried ($MgSO_4$) and concentrated. The resulting residue was subjected to flash column chromatography (silica gel) using petroleum spirit–dichloromethane (1:3) as an eluent to give the dione **8a**. Dark red powder; yield 58%; m.p.: 172 °C; IR (KBr): $\bar{\nu}$ = 1690, 1604, 1465, 1453, 1423, 1005, 762, 749, 718 cm^{-1}; $\lambda_{max/nm}$ (ε) = 247 (4000), 278 (4020) nm (M^{-1} cm^{-1}); ^1H NMR (400.1 MHz, $CDCl_3$): δ = 1.88 (br, 8H), 3.20 (t, J = 6.6 Hz, 4H), 3.83 (t, J = 6.8 Hz, 4H), 6.79 (d, J = 7.6 Hz, 2H), 6.93 (t, J = 4.8 Hz, 2H), 7.02–7.06 (m, 2H), 7.32–7.36 (m, 2H), 8.47 (d, J = 4.8 Hz, 4H), 9.15 (d, J = 7.4 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 25.6, 25.7, 29.3, 38.5, 106.8, 115.3, 120.6, 121.2, 128.9, 131.4, 132.4, 143.5, 156.1, 166.8, 171.3 ppm; HRMS (ESI): $[M+H]^+$ calcd for $C_{32}H_{31}N_6O_2S_2$ 595.1950, found 595.1946.

(*E*)-1,1′-Bis[5-(phenylsulfonyl)pentyl]-[3,3′-biindolinylidene]-2,2′-dione (10a, $C_{38}H_{38}N_2O_6S_2$) The mixture of 168 mg (*E*)-1,1′-bis(5-bromopentyl)-[3,3′-biindolinylidene]-2,2′-dione (**2e**, 0.3 mmol) and 164 mg sodium benzenesulfinate (**9**, 1 mmol) in 5 cm^3 DMF was stirred for 8 h at 70 °C. The resulting mixture was extracted with CH_2Cl_2 (2 × 10 cm^3), washed with 10 cm^3 water and the combined organic layers dried ($MgSO_4$) and concentrated. The resulting solid was subjected to flash column chromatography (silica gel) using petroleum ether–ethyl acetate (3:1) as an eluent and gave the dione **10a**. Dark red powder; yield 66%; m.p.: 154 °C; IR (KBr): $\bar{\nu}$ = 1692, 1604, 1461, 1443, 1417, 1251 1005, 782, 723 cm^{-1}; $\lambda_{max/nm}$ (ε) = 265 (3992), 395 (3439) nm (M^{-1} cm^{-1}); ^1H NMR (400.1 MHz, $CDCl_3$): δ = 1.41–1.49 (m, 4H), 1.65–1.80 (m, 8H), 3.06 (t, J = 7.8 Hz, 4H), 3.74 (t, J = 7.0 Hz, 4H), 6.73 (d, J = 7.7 Hz, 2H), 7.03 (td, J = 7.9, 0.8, 2H), 7.33 (td, J = 7.6, 0.9, 2H), 7.54 (t, J = 7.2 Hz, 4H), 7.61–7.65 (m, 2H), 7.86–7.88 (m, 4H), 9.10 (d, J = 7.4 Hz, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.4, 25.7, 27.0, 39.5, 55.9, 107.7, 121.6, 122.3, 128.0, 129.2, 129.9, 132.4, 133.3, 133.6, 139.0, 144.4, 167.8 ppm; HRMS (ESI): $[M+Na]^+$ calcd for $C_{38}H_{38}N_2O_6S_2Na$ 705.2069, found 705.2079.

(3*Z*,3′*Z*)-3,3′-(ethane-1,2-diylidene)bis(indolin-2-one) (12, $C_{18}H_{12}N_2O_2$) To a magnetically stirred solution of 2.00 g 2-oxindole (**11**, 15.00 mmol) in 8 cm^3 ethanol, 1.08 g glyoxal (40% w/w, 7.50 mmol) and 1 cm^3 concentrated hydrochloric acid were added and the mixture was heated for 6 h at reflux. After cooling, the mixture was filtered and the solid was washed with diethyl ether, ethyl acetate, and cold ethanol to give **12**. Red solid; yield 32%; m.p.: > 300 °C; IR (KBr): $\bar{\nu}$ = 1689, 1601, 1464, 1351, 1176, 749, 726 cm^{-1}; ^1H NMR (400.1 MHz, $CDCl_3$): δ = 6.85 (d, J = 7.7 Hz, 2H), 4.99 (t, J = 7.4 Hz, 2H), 7.27 (t, J = 7.6 Hz, 2H), 7.50 (d, J = 7.4 Hz, 2H), 8.79 (s, 2H), 10.68 (s, NH) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 110.4, 121.3, 122.1, 123.6, 127.6, 131.3, 131.8, 142.8, 168.4 ppm; HRMS (ESI): $[M+H]^+$ calcd for $C_{18}H_{13}N_2O_2$ 289.0977, found 289.0981.

General procedure for the synthesis of 13a–13c

To a magnetically stirred solution of (3*Z*,3′*Z*)-3,3′-(ethane-1,2-diylidene)bis(indolin-2-one) (**12**, 0.5 mmol) in 3 cm^3 DMF, sodium methoxide (1.1 mmol) was added in 2 cm^3 DMF at room temperature. The reaction mixture was stirred for 30 min, and then the alkyl bromide (3 mmol) was added and the mixture stirred for 8 h at 45 °C. The mixture was poured into 10 cm^3 H_2O, extracted with 20 cm^3 CH_2Cl_2, dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was subjected to silica gel column chromatography using petroleum spirit–ethyl acetate mixture as eluent.

(3*Z*,3′*Z*)-3,3′-(Ethane-1,2-diylidene)bis(1-isopropylindolin-2-one) (13a, $C_{24}H_{24}N_2O_2$) Red powder; m.p.: 184 °C; IR (KBr): $\bar{\nu}$ = 1689, 1601, 1464, 1351, 1176, 749, 726 cm^{-1}; $\lambda_{max/nm}$ (ε) = 228 (3018), 386 (3428) nm (M^{-1} cm^{-1}); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.52 (d, J = 7.0 Hz, 12H), 4.67 (sep, J = 6.9 Hz, 2H), 6.94 (d, J = 7.9 Hz, 2H), 7.00 (td, J = 7.5, 0.7 Hz, 2H), 7.22–7.27 (m, 2H), 7.63 (dd, J = 7.5, 0.5 Hz, 2H), 8.98 (s, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.5, 43.4, 109.7, 121.3, 121.7, 123.6, 128.5, 130.1, 131.1, 142.1, 166.8 ppm; HRMS (ESI): $[M+Na]^+$ calcd for $C_{24}H_{24}N_2O_2Na$ 395.1735, found 395.1723.

(3*Z*,3′*Z*)-3,3′-(Ethane-1,2-diylidene)bis[1-[(cyclohex-2-en-1-yl)methyl]indolin-2-one] (13b, $C_{30}H_{328}N_2O_2$) Red powder; m.p.: 188 °C; IR (KBr): $\bar{\nu}$ = 1690, 1600, 1464, 1351, 1176, 749, 670 cm^{-1}; $\lambda_{max/nm}$ (ε) = 279 (3754), 404 (3964) nm (M^{-1} cm^{-1}); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.71–1.78 (m, 2H), 1.89–1.95 (m, 6H), 2.09–2.11 (m, 4H), 5.09–5.12 (m, 2H), 5.58 (d, J = 12.0 Hz, 2H), 5.93–5.96 (m, 2H), 6.89–6.94 (m, 4H), 7.12 (td, J = 7.7, 1.1 Hz, 2H), 7.53 (d, J = 7.0 Hz, 2H), 8.93 (s, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.8, 24.5, 26.0, 47.9, 110.8, 121.1, 121.8, 123.5, 127.5, 128.7, 130.0, 130.9, 131.1, 142.1, 166.9 ppm; HRMS (ESI): $[M+Na]^+$ calcd for $C_{30}H_{328}N_2O_2Na$ 471.2048, found 471.2062.

(3*Z*,3′*Z*)-3,3′-(Ethane-1,2-diylidene)bis[1-(4-bromobutyl)indolin-2-one] (13c, $C_{26}H_{26}Br_2N_2O_2$) Red powder; m.p.: 156 °C; IR (KBr): $\bar{\nu}$ = 1690, 1608, 1465, 1356, 1331, 1150, 1095, 775, 743 cm^{-1}; $\lambda_{max/nm}$ (ε) = 234 (3952), 413 (4000) nm (M^{-1} cm^{-1}); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.85–1.98 (m, 8H), 3.47 (t, J = 6.3 Hz, 4H), 3.79 (t, J = 6.6 Hz, 4H), 6.81 (d, J = 7.8 Hz, 2H), 7.03 (td, J = 7.6, 0.8 Hz, 2H), 7.27–7.31 (m, 2H), 7.63 (dd, J = 7.5, 0.4 Hz, 2H), 8.97 (s, 2H) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.2, 29.8, 33.0, 38.6, 108.3, 121.4, 122.3, 123.3, 128.8, 130.5, 130.9, 142.7, 167.1 ppm; HRMS (ESI): $[M+Na]^+$ calcd for $C_{26}H_{26}^{79}Br_2N_2O_2Na$ 579.0259, found 579.0277.

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