Synthesis, characterisation and fluorescence studies of new bis-phenanthrimidazole derivatives

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The synthesis of new bis-phenanthrimidazole derivatives in one-pot four-component reaction from 9,10-phenanthraquinone, aromatic aldehydes, 4,4′-diaminodiphenyl ether and ammonium acetate is described. These new compounds were subsequently studied for their fluorescence properties.

Keywords: bis-phenanthrimidazoles, 1*H*-phenanthro[9,10-*d*]imidazol-2-yl, one-pot reaction, fluorescence, emission and absorption spectra

The 1*H*-phenanthro[9,10-*d*]imidazol-2-yl group is worth considering as a substituent in the field of molecular materials.[1] This group of compounds have also found application as a chromophore with high extinction coefficients, readily tunable absorption wavelengths, and fluorophoric properties and are useful as large planar synthetic building blocks in supramolecular chemistry. Besides early reports[2] of its synthesis from 9,10-phenanthraquinone and an aromatic aldehyde, the system has received little interest.

Fluorescence is a highly sensitive and convenient method of detection that has significantly influenced the landscape of molecular biotechnology over the past few decades. An increasingly wide variety of fluorophores is used in biotechnology, genomics, immunoassays, array technologies, imaging, and drug discovery.[3,4]

Fluorescent molecules can easily be attached to a cast of target molecules, including DNA, RNA, antibodies, peptides, and proteins, and have the distinct advantage of being small compared to several other molecular labels. Fluorescence-based technologies are used in a wide variety of biotechnology applications, including automated DNA sequencing, real-time PCR, microarray analyses, and immunoassays. It has been shown that the fluorescent dyes which have a small size, establish little interference with the properties of the labelled molecule and infiltration to the cellular regions is readily accomplished.[5,6]

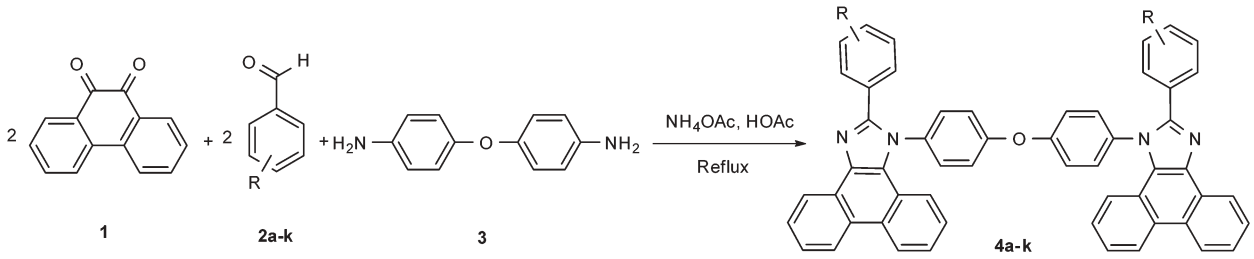
Organic fluorophores or fluorescent dyes are characterised by a strong absorption and emission band in the visible region of the electromagnetic spectrum. Fluorescent heterocyclic compounds are of interest as functional materials in many disciplines such as emitters for electroluminescence devices,[7] molecular probes for biochemical research,[8] in traditional textile and polymer fields,[9] as whitening agents[10] and in photoconducting materials.[11]

In the present study, we describe the synthesis of new bis-phenanthrimidazole derivatives, which have fluorescence properties, from 9,10-phenanthraquinone, various aromatic aldehydes, 4,4′-diaminodiphenyl ether and ammonium acetate in acetic acid (Scheme 1).

Results and discussion

The new bis-phenanthrimidazole derivatives **4a–k** were synthesised *via* a one-pot four-component reaction from 9,10-phenanthraquinone, aromatic aldehydes, 4,4′-diaminodiphenyl ether and ammonium acetate in acetic acid (Scheme 1).

The structures of compounds **4a–k** were characterised by elemental, FTIR, ^{1}H and ^{13}C NMR analyses.



4a: R = H
4b: R = 4-Me
4c: R = 4-OMe
4d: R = 4-NO_2
4e: R = 2-NO_2
4f: R = 4-Cl
4g: R = 4-F
4h: R = 3,4-dimethoxy
4i: R = 4-bromo
4j: R = 4-cyano
4k: R = 2,4-dichloro

Scheme 1

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Table 1 Photophysical data for absorption and fluorescence of **4a–k**

Compound	4a	4b	4c	4d	4e	4f	4g	4h	4i	4j	4k
λ_{abs} /nm[a]	260	262	260	260	258	262	261	261	374	361	366
$\varepsilon \times 10^{-6}$ /mol^{-1} L cm^{-1} [b]	4.0	3.0	2.0	2.5	2.5	3.5	3.0	4.0	3.5	3.5	3.0
λ_{ex} /nm[c]	260	262	260	260	258	262	261	261	374	361	366
λ_{flu}/nm[d]	369	382	393	435	435	384	380	386	392	418	386
Φ_F[e]	1.24	0.95	1.00	0.80	0.77	0.84	0.89	1.10	0.70	19.35	0.80

[a] Wavelengths of maximum absorbance.
[b] Extinction coefficient.
[c] Wavelengths of fluorescence excitation.
[d] Wavelengths of fluorescence emission.
[e] Fluorescence quantum yield (%).

In order to study the fluorescence properties of these new compounds, we investigated the fluorescence absorption and emission spectra of compounds **4a–k**. The λ_{abs}, values of extinction coefficient (ε), λ_{ex}, λ_{flu} and fluorescence quantum yield (Φ_F) data of these compounds are presented in Table 1. Values of the extinction coefficient (ε) were calculated from the slope of the plot of absorbance *versus* concentration. The fluorescence quantum yields (Φ_F) of compounds **4a–k** were determined using comparison methods, with fluorescein as a standard sample in 0.1 M NaOH and MeOH solution.[12] It can be concluded from the data in Table 1 that these novel compounds are fluorescent. A typical photoinduced charge transfer system consists of a donor (D) and acceptor (A) couple, which can be separate chromophores within a large molecule, leading to intramolecular charge transfer (ICT). Overlap of the imidazole ring nitrogen with the π-system affords a highly conjugated array. For example in **4j** this occurs from ring-N through to the acceptor nitrile group centre, as depicted in Scheme 2.

The fluorescence absorption and emission spectra of compound **4j** which had the highest quantum yield (Φ_F), were measured at the concentration of 1×10^{-6} mol L^{-1} in several solvents (Figs 1 and 2). As is demonstrated in these figures, the fluorescence absorption and emission spectra of **4j** in polar solvents exhibited a solvatochromic red shift with increasing solvent polarity. Solvent effects shift the emission to lower energy owing to stabilisation of the excited state by the polar solvent molecules (Table 2). This type of behavior is observed for most of the dyes. For example, in Table 2, one can see that in the absorption spectrum for **4j**, λ_{abs} shifts from 358 to 364 nm, and in the emission spectrum, λ_{flu} shifts from 410 to 436 nm as the solvent is changed from *n*-hexane to methanol.

In conclusion, we have successfully synthesised and characterised new bis-phenanthrimidazole derivatives which have fluorescence properties; research into their possible applications is in progress and will be reported elsewhere.

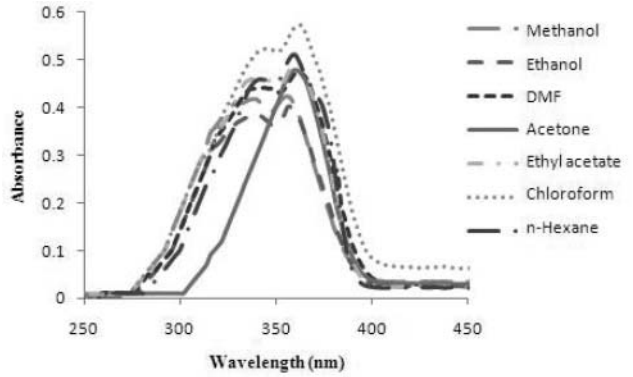


Fig. 1 Visible absorption spectrum of compound **4j** in some solvents (1×10^{-6} mol L^{-1}).

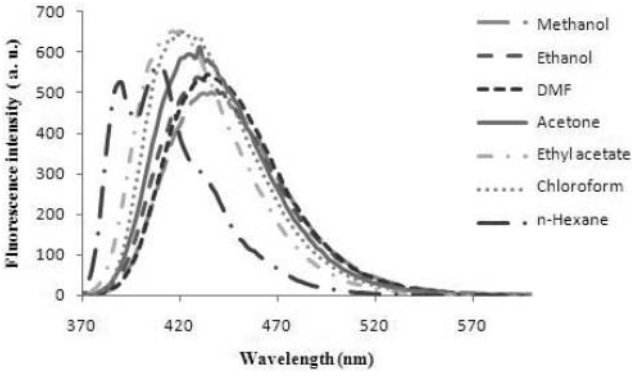
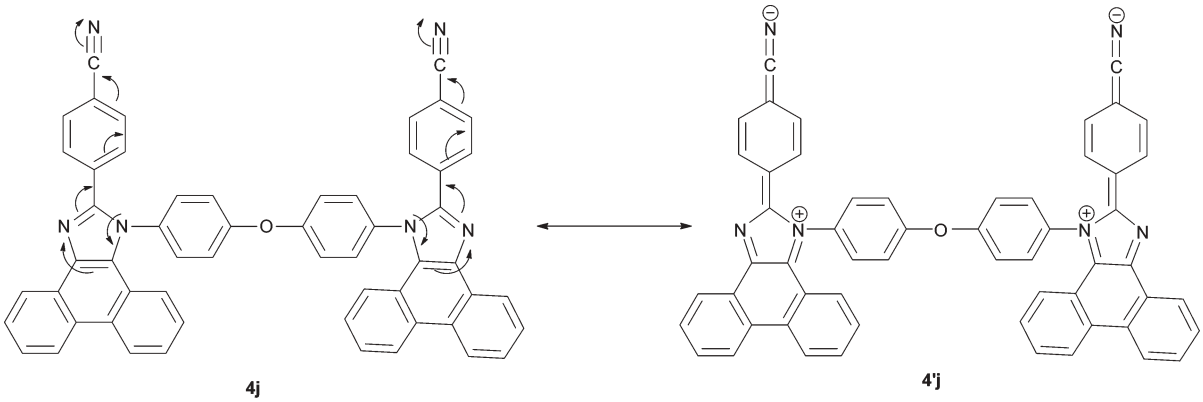


Fig 2 Emission spectrum of compound **4j** in some solvents (1×10^{-6} mol L^{-1}).



4j **4'j**

Scheme 2

Table 2 Spectroscopic data for **4j** at 298 K in dependence of the solvent

Solvent	λ_{abs}/nm	λ_{flu}/nm
n-Hexane	358	410
Chloroform	360	420
Ethyl acetate	360	420
Acetone	361	430
DMF	362	433
Ethanol	362	434
Methanol	364	436

Experimental

Chemicals were either prepared in our laboratories or purchased from Merck, Fluka, and Aldrich Chemical Companies. All yields refer to isolated products. Melting points were recorded on an Electrothermal type 9100 melting point apparatus. The IR spectrometer used was Bruker Tensor 27. The IR spectra were taken using KBr pellets. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker spectrometer. The mass spectra were scanned on a Varian Mat CH-7 instrument at 70 eV. Absorption and fluorescence spectra were recorded on a Varian 50-bio UV–Vis spectrophotometer and a Varian Cary Eclipse spectrofluorophotometer. UV–Vis and fluorescence scans were recorded from 350 to 700 nm.

Synthesis of **4a–k**; *general procedure*

A mixture of an aldehyde (2.0 mmol), 9,10-phenanthraquinone (2.0 mmol), 4,4′-diaminodiphenyl ether (1.0 mmol) and ammonium acetate (2.0 mmol) in acetic acid (5 mL) was heated at 120 °C. The progress of reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature. Then the product was filtered, washed with water and recrystallised from ethanol to the following compounds.

*1-{4-[4-(2-Phenyl-1*H*-phenanthro[9,10-*d*]imidazol-1-yl)phenoxy]-phenyl}-2-phenyl-1*H*-phenanthro[9,10-*d*]imidazole* (**4a**): Light pink powder; reaction time: 45 min; yield: 90%; m.p. 343–345 °C; IR: ν_{max}/cm^{-1}; 3070, 1605, 1500, 850; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.35 (m, 14H), 7.51–7.57 (m, 6H), 7.63–7.65 (m, 4H), 7.67 (t, 2H, *J* = 7.2 Hz), 7.76 (t, 2H, *J* = 7.2 Hz), 8.71 (d, 2H, *J* = 8.4 Hz), 8.79 (d, 2H, *J* = 8.4 Hz), 8.89 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz), δ 120.25, 120.68, 122.80, 123.02, 123.16, 124.29, 125.01, 125.74, 126.34, 127.24, 127.39, 127.85, 128.16, 128.33, 129.02, 129.38, 129.55, 130.53, 130.94, 134.44, 137.51, 151.21, 157.21; MS, *m/z*: 754. Anal. Calcd for $C_{54}H_{34}N_4O$: C, 85.92; H, 4.54; N, 7.42. Found: C, 85.80; H, 4.61; N, 7.35%.

*1-{4-[4-(2-*p*-Tolyl-1*H*-phenanthro[9,10-*d*]imidazol-1-yl)phenoxy]-phenyl}-2-*p*-tolyl-1*H*-phenanthro[9,10-*d*]imidazole* (**4b**): Light violet powder; reaction time: 35 min; yield: 92%; m.p. >350 °C; IR: ν_{max}/cm^{-1}; 3065, 1596, 1503, 845; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 6H, $2CH_3$), 7.14 (d, 4H, *J* = 8.4 Hz), 7.32–7.35 (m, 8H), 7.51–7.58 (m, 10H), 7.66 (t, 2H, *J* = 7.2 Hz), 7.75 (t, 2H, *J* = 7.2 Hz), 8.71 (d, 2H, *J* = 8.0 Hz), 8.79 (d, 2H, *J* = 8.0 Hz), 8.88 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz), δ 21.39, 120.26, 120.63, 122.79, 123.04, 123.14, 124.28, 124.90, 125.67, 126.30, 127.22, 127.36, 127.60, 128.08, 128.25, 129.06, 129.29, 129.38, 130.48, 130.95, 134.56, 137.45, 151.36, 157.19; MS, *m/z*: 782. Anal. Calcd for $C_{56}H_{38}N_4O$: C, 85.91; H, 4.89; N, 7.16. Found: C, 85.75; H, 4.73; N, 7.20%.

*1-{4-[4-(2-(4-Methoxyphenyl)-1*H*-phenanthro[9,10-*d*]imidazol-1-yl)-phenoxy]phenyl}-2-(4-methoxyphenyl)-1*H*-phenanthro[9,10-*d*]imidazole* (**4c**): Light violet powder; reaction time: 35 min; yield: 92%; m.p. 308–310 °C; IR: ν_{max}/cm^{-1}; 3055, 1590, 1495, 853; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 6H, $2CH_3$), 6.86 (d, 4H, *J* = 8.4 Hz), 7.32–7.35 (m, 8H), 7.50–7.58 (m, 10H), 7.66 (t, 2H, *J* = 7.2 Hz), 7.75 (t, 2H, *J* = 7.2 Hz), 8.71 (d, 2H, *J* = 8.0 Hz), 8.79 (d, 2H, *J* = 8.0 Hz), 8.87 (d, 2H, *J* = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz), δ 55.30, 113.79, 120.27, 120.58, 122.76, 122.94, 123.03, 123.14, 124.27, 124.83, 125.63, 126.29, 127.20, 127.33, 127.98, 128.23, 129.23, 130.92, 130.99, 134.62, 137.39, 151.23, 157.18, 160.17; MS, *m/z*: 814. Anal. Calcd for $C_{56}H_{38}N_4O_3$: C, 82.54; H, 4.70; N, 6.88. Found: C, 82.84; H, 4.65; N, 6.81%.

*1-{4-[4-(2-(4-Nitrophenyl)-1*H*-phenanthro[9,10-*d*]imidazol-1-yl)-phenoxy]phenyl}-2-(4-nitrophenyl)-1*H*-phenanthro[9,10-*d*]imidazole* (**4d**): Dark green powder; reaction time: 35 min; yield: 90%; m.p. >350 °C; IR: ν_{max}/cm^{-1}; 3058, 1596, 1574, 1499, 1340, 855; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, 2H, *J* = 8.8 Hz), 7.35 (d, 2H, *J* = 7.2 Hz), 7.44 (d, 4H, *J* = 8.8 Hz), 7.57 (t, 2H, *J* = 7.2 Hz), 7.64 (d, 4H, *J* = 8.8 Hz), 7.70 (t, 2H, *J* = 7.2 Hz), 7.75–7.82 (m, 6H), 8.12 (d, 4H, *J* = 8.8 Hz), 8.71 (d, 2H, *J* = 8.0 Hz), 8.79 (d, 2H, *J* = 8.0 Hz), 8.85 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz), δ 120.67, 120.78, 122.68, 122.73, 123.27, 123.53, 124.45, 125.69, 126.27, 126.54, 126.93, 127.65, 128.53, 129.02, 129.78, 129.88, 130.88, 134.09, 136.52, 137.97, 147.51, 148.22, 157.45; MS, *m/z*: 844. Anal. Calcd for $C_{54}H_{32}N_6O_5$: C, 76.77; H, 3.82; N, 9.95. Found: C, 76.84; H, 3.75; N, 9.89%.

*1-{4-[4-(2-(2-Nitrophenyl)-1*H*-phenanthro[9,10-*d*]imidazol-1-yl)-phenoxy]phenyl}-2-(2-nitrophenyl)-1*H*-phenanthro[9,10-*d*]imidazole* (**4e**): Dark green powder; reaction time: 50 min; yield: 88%; m.p. 316–318 °C; IR: ν_{max}/cm^{-1}; 3060, 1596, 1570, 1499, 1352, 850; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, 4H, *J* = 8.8 Hz), 7.31(d, 2H, *J* = 8.0 Hz), 7.35 (d, 2H, *J* = 8.0 Hz), 7.43 (d, 4H, *J* = 8.8 Hz), 7.55 (d, 2H, *J* = 7.2 Hz), 7.59 (d, 2H, *J* = 7.2 Hz), 7.65–7.75 (m, 8H), 8.04 (d, 2H, *J* = 8.0 Hz), 8.73 (d, 2H, *J* = 8.4 Hz), 8.76 (d, 2H, *J* = 8.4 Hz), 8.80 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz), δ 119.95, 120.75, 122.72, 122.79, 123.19, 124.32, 124.69, 125.36, 125.89, 126.41, 127.05, 127.50, 127.67, 128.38, 129.54, 130.39, 130.72, 132.70, 133.19, 137.64, 147.79, 148.90, 156.96; MS, *m/z*: 844. Anal. Calcd for $C_{54}H_{32}N_6O_5$: C, 76.77; H, 3.82; N, 9.95. Found: C, 76.89; H, 3.78; N, 9.98%.

*1-{4-[4-(2-(4-Chlorophenyl)-1*H*-phenanthro[9,10-*d*]imidazol-1-yl)-phenoxy]phenyl}-2-(4-chlorophenyl)-1*H*-phenanthro[9,10-*d*]imidazole* (**4f**): Light violet powder; reaction time: 35 min; yield: 90%; m.p. 318–320 °C; IR: ν_{max}/cm^{-1}; 3060, 1593, 1497, 848; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, 6H, *J* = 8.8 Hz), 7.37 (d, 6H, *J* = 8.8 Hz), 7.53 (d, 2H, *J* = 7.2 Hz), 7.58 (d, 8H, *J* = 8.8 Hz), 7.67 (t, 2H, *J* = 7.2 Hz), 7.76 (t, 2H, *J* = 7.2 Hz), 8.72 (d, 2H, *J* = 8.0 Hz), 8.79 (d, 2H, *J* = 8.0 Hz), 8.85 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz), δ 120.40, 120.64, 122.73, 122.90, 123.19, 124.34, 125.17, 125.88, 126.39, 127.10, 127.47, 128.34, 128.63, 128.99, 129.48, 130.70, 130.91, 134.29, 135.22, 137.53, 147.50, 149.96, 157.26; MS, *m/z*: 823. Anal. Calcd for $C_{54}H_{32}Cl_2N_4O$: C, 78.73; H, 3.92; N, 6.80. Found: C, 78.90; H, 3.86; N, 6.93%.

*1-{4-[4-(2-(4-Fluorophenyl)-1*H*-phenanthro[9,10-*d*]imidazol-1-yl)-phenoxy]phenyl}-2-(4-fluorophenyl)-1*H*-phenanthro[9,10-*d*]imidazole* (**4g**): Light violet powder; reaction time: 35 min; yield: 90%; m.p. >350 °C; IR: ν_{max}/cm^{-1}; 3060, 1596, 1495, 850; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (t, 4H, *J* = 8.8 Hz), 7.30 (d, 4H, *J* = 8.8 Hz), 7.35 (d, 4H, *J* = 8.8 Hz), 7.52–7.64 (m, 10H), 7.67 (t, 2H, *J* = 7.2 Hz), 7.76 (t, 2H, *J* = 7.2 Hz), 8.72 (d, 2H, *J* = 8.0 Hz), 8.79 (d, 2H, *J* = 8.0 Hz), 8.85 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz), δ 115.39, 120.33, 120.61, 122.72, 123.18, 124.33, 125.08, 125.82, 126.36, 126.67, 127.12, 127.45, 128.15, 128.31, 129.41, 130.93, 131.45, 131.53, 134.32, 150.26, 157.21, 161.88, 164.36; MS, *m/z*: 790. Anal. Calcd for $C_{54}H_{32}F_2N_4O$: C, 82.01; H, 4.08; N, 7.08. Found: C, 82.20; H, 4.14; N, 7.03%.

*1-{4-[4-(2-(3,4-Dimethoxyphenyl)-1*H*-phenanthro[9,10-*d*]imidazol-1-yl)phenoxy]phenyl}-2-(3,4-dimethoxyphenyl)-1*H*-phenanthro-[9,10-*d*]imidazole* (**4h**): Dark brown powder; reaction time: 50 min; yield: 89%; m.p. 198–200 °C; IR: ν_{max}/cm^{-1}; 3066, 1596, 1500, 852; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 12H, $4CH_3$), 6.79 (d, 2H, *J* = 8.4 Hz), 7.12 (d, 2H, *J* = 8.4 Hz), 7.31–7.36 (m, 10H), 7.52 (t, 2H, *J* = 7.6 Hz), 7.59 (d, 4H, *J* = 8.4 Hz), 7.66 (t, 2H, *J* = 7.6 Hz), 7.75 (t, 2H, *J* = 7.6 Hz), 8.71 (d, 2H, *J* = 8.4 Hz), 8.78 (d, 2H, *J* = 8.4 Hz), 8.88 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz), δ 55.90, 120.26, 120.57, 122.39, 122.77, 122.98, 123.17, 124.230, 124.91, 125.71, 126.31, 127.13, 127.38, 128.04, 128.27, 129.28, 129.54, 131.05, 134.78, 137.31, 148.63, 149.77, 151.06, 157.19; MS, *m/z*: 874. Anal. Calcd for $C_{58}H_{42}N_4O_5$: C, 79.62; H, 4.84; N, 6.40. Found: C, 79.70; H, 4.77; N, 6.48%.

*1-{4-[4-(2-(4-Bromophenyl)-1*H*-phenanthro[9,10-*d*]imidazol-1-yl)-phenoxy]phenyl}-2-(4-bromophenyl)-1*H*-phenanthro[9,10-*d*]imidazole* (**4i**): Grey powder; reaction time: 45 min; yield: 85%; m.p. >350 °C; IR: ν_{max}/cm^{-1}; 3058, 1600, 1499, 855; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.58 (m, 16H), 7.61(d, 6H, *J* = 8.4 Hz), 7.71 (t, 2H, *J* = 7.2 Hz), 7.78 (t, 2H, *J* = 7.2 Hz), 8.74 (d, 2H, *J* = 8.4 Hz), 8.82 (d, 2H, *J* = 8.4 Hz), 8.90 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz), δ 120.44, 120.66, 122.78, 122.83, 123.19, 123.74, 124.36, 125.30, 126.01, 126.46, 127.55, 128.27, 128.38, 129.53, 130.90, 130.99,

131.62, 134.14, 157.28; MS, *m/z*: 912. Anal. Calcd for $C_{54}H_{32}Br_2N_4O$: C, 71.06; H, 3.53; Br, 17.51; N, 6.14; O, 1.75. Found: C, 71.10; H, 3.58; Br, 17.50; N, 6.10; O, 1.72%.

*1-{4-[4-(2-(4-Cyanophenyl)-1*H*-phenanthro[9,10-*d*]imidazol-1-yl)-phenoxy]phenyl}-2-(4-cyanophenyl)-1*H*-phenanthro[9,10-*d*]imidazole* (**4j**): Grey powder; reaction time: 25 min; yield: 88%; m.p. >350 °C; IR: ν_{max}/cm^{-1}; 3058, 2223, 1606, 1498, 1238, 844; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, 2H, *J* = 8.4 Hz), 7.38 (t, 2H, *J* = 7.2 Hz), 7.45 (d, 4H, *J* = 8.4 Hz), 7.60 (t, 2H, *J* = 7.2 Hz), 7.64–7.68 (m, 8H), 7.73 (t, 2H, *J* = 7.2 Hz), 7.78–7.83 (m, 6H), 8.74 (d, 2H, *J* = 8.4 Hz), 8.82 (d, 2H, *J* = 8.4 Hz), 8.90 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz), δ 112.53, 118.40, 120.63, 120.75, 122.60, 122.86, 123.26, 124.47, 125.72, 126.36, 126.57, 127.72, 128.53, 128.75, 129.76, 130.87, 132.10, 133.91, 148.44, 157.43; MS, *m/z*: 805. Anal. Calcd for $C_{56}H_{32}N_6O$: C, 83.56; H, 4.01; N, 10.44; O, 1.99. Found: C, 83.48; H, 4.05; N, 10.42; O, 2.05%.

*1-(4-(4-(2-(2,4-Dichlorophenyl)-1*H*-phenanthro[9,10-*d*]imidazol-1-yl)phenoxy)phenyl)-2-(2,4-dichlorophenyl)-1*H*-phenanthro[9,10-*d*]-imidazole* (**4k**): Light brown powder; reaction time: 30 min; yield: 87%; m.p. 218–220 °C; IR: ν_{max}/cm^{-1}; 3062, 1600, 1502, 1243; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, 4H, *J* = 8.4 Hz), 7.32–7.49 (m, 10H), 7.52 (d, 4H, *J* = 8.4 Hz), 7.60 (t, 2H, *J* = 7.2 Hz), 7.70 (t, 2H, *J* = 7.2 Hz), 7.77 (t, 2H, *J* = 7.2 Hz), 8.75 (d, 2H, *J* = 8.4 Hz), 8.85 (t, 4H, *J* = 9.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz), δ 119.80, 120.78, 122.62, 122.85, 123.20, 124.33, 125.47, 126.03, 126.47, 126.95, 127.37, 127.61, 128.38, 128.70, 129.58, 130.14, 133.57, 135.97, 136.62, 148.03, 156.98; MS, *m/z*: 892. Anal. Calcd for $C_{54}H_{30}Cl_4N_4O$: C, 72.66; H, 3.39; Cl, 15.89; N, 6.28; O, 1.79. Found: C, 72.73; H, 3.42; Cl, 15.83; N, 6.25; O, 1.77%.

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