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THE EXTENSION OF CONJUGATED SYSTEM IN PYRIDYL-SUBSTITUTED MONOAZATRIPHENYLENES FOR THE TUNING OF PHOTOPHYSICAL PROPERTIES

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We propose a method for the synthesis of diaryl-substituted pyridylmonoazatriphenylenes by the heterocyclization reaction of dihalosubstituted phenanthrenequinones with pyridine-2-carboxylic acid amidrazone, followed by aza-Diels–Alder reaction and Suzuki cross coupling. The obtained compounds showed more promising photophysical properties, compared to non-arylated analogs.

Keywords: monoazatriphenylene, phenanthrenequinone, aza-Diels–Alder reaction, cross coupling, heterocyclization, luminescence, Suzuki reaction.

Azatriphenylene (dibenzo[*f*,*h*]quinoline) structures, which are of interest due to their remarkable photophysical and coordination properties [1], have been found in several natural compounds [2, 3]. Azatriphenylenes and their annelated derivatives are used in the inorganic biochemistry as intercalating ligands – components of luminescent metal complexes – for the study of DNA structure and its defragmentation [4, 5]. Azatriphenylenes are also promising luminescent sensors for organic anions and nitroaromatic compounds [6].

Of particular interest are pyridyl-substituted azatriphenylenes, which are polycyclic 2,2'-bipyridine ligands with broad possibilities for further functionalization. It has been previously shown that extending the conjugated system of 2,2'-bipyridines [7, 8], 1,10-phenanthrolines [9, 10], and 2,2':6',2"-terpyridines [11, 12] may be used for the tuning of photophysical characteristics of these compounds. For example, the absorption and luminescence maxima may be shifted to the longer wavelengths, and the quantum yield of luminescence may be increased, improving the potential for practical applications of these compounds. These properties of pyridylmonoazatriphenylenes currently remain unexplored, as only very few chemical structures of this type have been synthesized so far. In this article, we propose a method for the synthesis of 2,2'-bipyridine ligands with extended conjugated system by introducing additional aromatic substituents in the monoazatriphenylene system.

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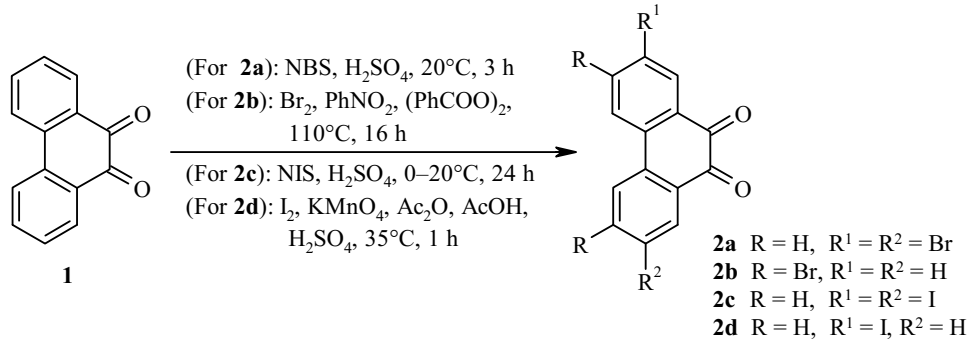
The most frequently used methods for the preparation of azatriphenylenes are the Skraup synthesis [13-16], various heterocyclization reactions [17-19], and cross-coupling reactions [20]. Another method involves the cycloaddition of difficult to obtain alkenes or arylacetylenes with aromatic substrates, which is catalyzed by transition metal salts [21]. These methods often require the use of forcing conditions or scarce reagents. In addition, we should note the preparation of monoazatriphenylenes through their 1,2,4-triazine analogs (this method often allows to prepare various substituted pyridines, unavailable by other methods [22-24]). Such a method is applicable to the monoazatriphenylene series in cases of intramolecular Diels–Alder reactions of the corresponding triazatriphenylenes with acetylene moieties [25]. Besides that, we recently described the synthesis of pyridylmonoazatriphenylenes by preparing their 1,2,4-triazine analogs with further aza-Diels–Alder reaction with enamines [26], relying on the use of commercially available reagents. The scope of our work includes the development of this direction.

One of the starting compounds for the preparation of target structures in this case was 9,10-phenanthrene quinone (**1**), with a range of methods currently known for its functionalization. Thus, its various derivatives may be used in the heterocyclization reaction with amidrazones, leading to 1,2,4-triazine analogs of functionalized azatriphenylenes.

For example, the bromination of phenanthrenequinone with *N*-bromosuccinimide (NBS) in sulfuric acid may produce 2,7-dibromophenanthrenequinone **2a** [27]. The iodination of phenanthrenequinone with *N*-iodosuccinimide (NIS) in sulfuric acid allows to synthesize 2,7-diiodophenanthrenequinone **2c** (this method of iodination [28] was earlier proposed for fluorenone, but has not been used for the preparation of compound **2c**). It should be noted that halogenation at positions 2 and 7 occurs with a high degree of selectivity, according to the electrophilic substitution rules in aromatic systems. An alternative method for the preparation of compound **2c** [29] by using molecular iodine under oxidative conditions (experiments with potassium permanganate and manganese dioxide were performed), contrary to literature data about the formation of 2,7-diiodophenanthrenequinone **2c** under these conditions, unexpectedly gave the 2-iodophenanthrenequinone **2d**, also of interest as a starting material for the synthesis of azatriphenylenes. The structure of compound **2d** was established by mass spectrometry data, and also by comparing its ^{1}H NMR spectrum with the literature data [30].

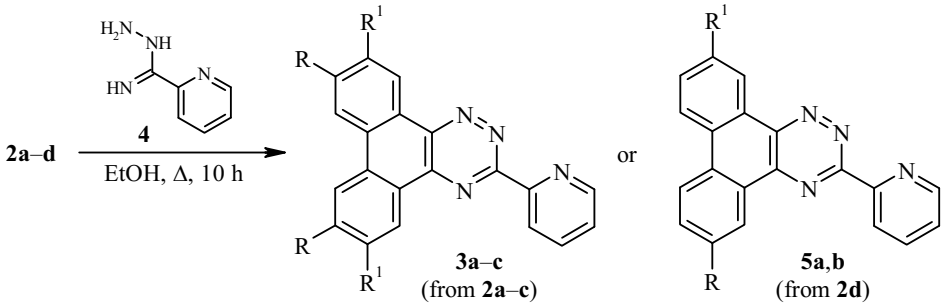
In addition to 2,7-dihalo-substituted quinones, the isomeric 3,6-dibromoquinone **2b** may be obtained in the reaction of phenanthrenequinone **1** with bromine in nitrobenzene in the presence of benzoyl peroxide [31].



It is obvious that after heterocyclization and aza-Diels–Alder reaction the halogen atoms in the molecule of monoazatriphenylene may be substituted in various ways, in order to tune the properties of target compounds. It should also be noted that dibenzo[*f,h*]quinolines with halogen atoms at positions 6 and 11 may be used as monomer units for the synthesis of various polymers. Monoiodo derivative in such a case presents interest as the capping monomer for obtaining polymers of limited chain length.

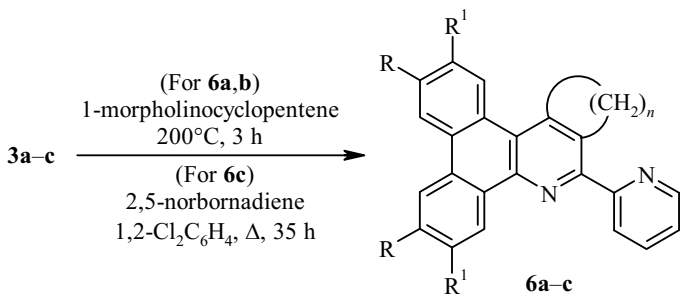
Despite the availability of halogenated phenanthrenequinones, only in few cases these compounds have been used for the preparation of the respective triazatriphenylenes [32-34], while no examples are known in the literature for obtaining similar monoazatriphenylenes in aza-Diels–Alder reactions.

The synthesis of triazatriphenylenes (3-(2-pyridyl)phenanthro[9,10-*e*][1,2,4]triazines) **3a-c** by the reactions of phenanthrenequinone derivatives **2a-c** with amidrazone **4** [35] is relatively smooth: heterocyclization occurs upon refluxing in ethanol. The reaction products may be easily isolated from the reaction mixture on account of their lower solubility in comparison to the starting materials, and the yields reach 64%. In the case of 2-iodophenanthrenequinone **2d**, the formation of two isomers **5a** and **5b** is observed in this reaction, in a ratio close to 1:1. The separation of these isomers is not considered necessary, taking into account the possible use of similar compounds as capping agents for polymers.



3 a R = H, R^1 = Br; **b** R = Br, R^1 = H; **c** R = H, R^1 = I; 5 **a** R = I, R^1 = H; **b** R = H, R^1 = I

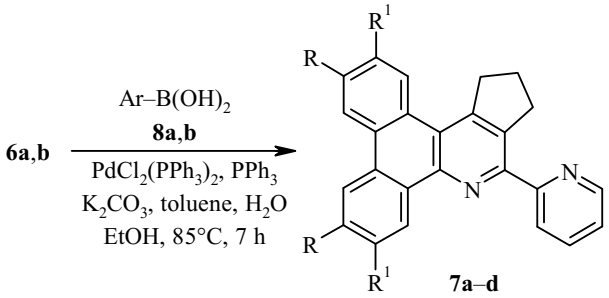
The further aza-Diels–Alder reaction using the previously described [36, 37] efficient procedure (interaction of 1,2,4-triazine with 1-morpholinocyclopentene at 200°C under inert atmosphere without solvent) was used for obtaining monoazatriphenylenes annelated with a cyclopentane ring – 10-(2-pyridyl)-12,13-dihydro-11*H*-dibenzo[*f*,*h*]cyclopenta[*c*]quinolines **6a-c**. Such compounds are potentially more useful, due to better solubility compared to non-annelated analogs. In the case of dibromo-substituted triazatriphenylenes **3a**,**b**, this procedure allowed to successfully obtain the target monoazatriphenylenes **6a**,**b** in up to 82% yields. Different results were obtained with the analogous iodo derivatives. A complex mixture of products was obtained when reacting a mixture of compounds **5a** and **5b**, as well as compound **3c** with enamine under the conditions described above. This was probably linked to the partial exchange of iodine atoms for amine fragments. Performing the reaction in high-boiling solvents (1,2-dichlorobenzene, *o*-xylene) also did not allow to obtain the desired iodo-containing cyclopentenomonoazatriphenylene. For example, prolonged refluxing in *o*-xylene resulted in the isolation of unchanged starting materials. In particular, in the case of iodo-containing triazatriphenylenes, significant difficulties are encountered when attempting the synthesis of 2,2'-bipyridine analogs annelated with cyclopentane ring. The preparation of the monoazatriphenylene diiodo derivative **6c** was eventually possible only by performing the aza-Diels–Alder reaction with 2,5-norbornadiene. This compound was deemed to have less practical potential, as its solubility is lower. Thus, if triazatriphenylene iodo derivatives are used, it is probably advantageous to substitute the labile iodine atoms for other functional groups prior to performing the aza-Diels–Alder reaction.



6 a R = H, R^1 = Br, n = 3
b R = Br, R^1 = H, n = 3
c R = H, R^1 = I, n = 0

The ^{1}H NMR spectra of the obtained compounds featured signals of azatriphenylene ABX systems (and also AB system signals in the case of compound **6c**), pyridine ring signals, but in the case of the monoazatriphenylenes **6a**,**b** also aliphatic proton signals due to the cyclopentene fragment.

The monoazatriphenylene dibromo derivatives **6a**,**b** were used as starting compounds for obtaining the target molecules **7a-d** with an extended conjugated system. The synthesis was performed by Suzuki cross-coupling reaction with the arylboronic acids **8a**,**b** in a mixture of water, toluene, and ethanol. Potassium carbonate was used as base, the cross-coupling products were obtained in high yields and were purified by recrystallization from toluene.



7a R = H; R^1 = Ph
b R = H, R^1 = 3,4,5-$(MeO)_3C_6H_2$
c R = Ph; R^1 = H
d R = 3,4,5-$(MeO)_3C_6H_2$; R^1 = H
8a Ar = Ph,
b Ar = 3,4,5-$(MeO)_3C_6H_2$

The photophysical properties of the obtained pyridylmonoazatriphenylenes were studied in comparison to our previously described unsubstituted 10-(2-pyridyl)-12,13-dihydro-11*H*-dibenzo[*f*,*h*]cyclopenta[*c*]-quinoline (**7e**) [26]. The luminescence spectra are presented in Figure 1, results are given in Table 1.

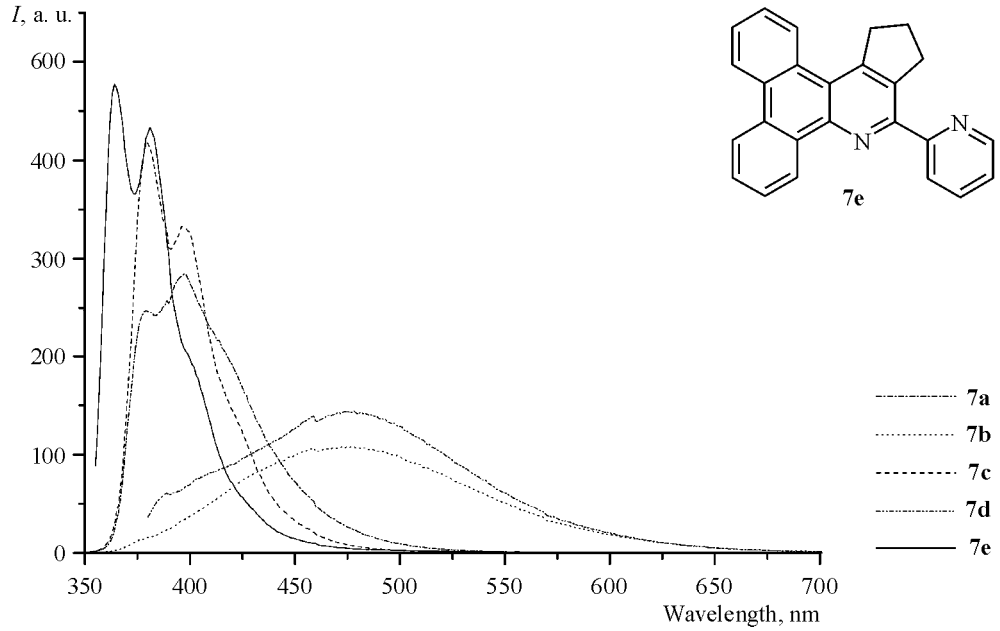


Fig. 1. Luminescence spectra of the pyridylmonoazatriphenylenes **7a-e** in acetonitrile at room temperature.

The study of photophysical properties indicated a shift of absorption and emission maxima towards the longer wavelengths due to the extension of the conjugated system. In the case of compounds **7a**,**c** (with phenyl substituents), the overall shape of luminescence spectrum remained practically unchanged, except that a bathochromic shift of emission maxima was noted. For compounds **7b**,**d** (with trimethoxyphenyl substituents),

TABLE 1. Photophysical Characteristics of Compounds **7a-e**

Compound	Absorption maxima in acetonitrile, nm	Luminescence maximum in acetonitrile, nm	Quantum yield of luminescence*
7a	289, 318	379, 398	0.207
7b	200, 294, 323	475	0.139
7c	193, 281, 325, 368	379, 396, 423 (sh)	0.146
7d	207, 284, 328, 370	481	0.216
7e	263, 313, 339, 357	364, 381, 403 (sh)	0.213

*The quantum yields of all compounds were measured relative to quinine sulfate (Φ = 0.546 in 0.1 N aqueous H_2SO_4 solution [38]).

substantial changes in the character of emission spectrum were observed, along with a larger bathochromic shift of emission maximum, which likely could be explained by the more substantial changes in chromophore structure. The quantum yields were somewhat lower in the case of compounds **7b**,**c**, while for the two other new monoazatriphenylenes the quantum yields remained practically unchanged.

Thus, we propose convenient methods for the preparation of previously unreported monoazatriphenylene diaryl derivatives of practical interest, based on the use of commercially available starting materials. These compounds were obtained by halogenation of 9,10-phenanthrenequinone followed by a heterocyclization reaction, aza-Diels–Alder reaction, and Suzuki cross coupling. Limitations for using iodine derivatives as intermediates were identified, and the advantages of bromine derivatives were demonstrated. The photophysical properties of the obtained compounds were examined in comparison to our previously reported unsubstituted analog. The more promising photophysical properties of aryl derivatives were demonstrated, manifested as bathochromic shifts of absorption and emission maxima, due to the extended conjugated system in these monoazatriphenylenes.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were acquired on a Bruker Avance II instrument (400 and 100 MHz, respectively) in $CDCl_3$ (compounds **6a**,**b**, **7a-d**) and in DMSO-d_6 (the rest of the compounds), internal standard was TMS. Absorption spectra were recorded on a Shimadzu UV-2401PC spectrophotometer in acetonitrile. Luminescence spectra were recorded on a Varian Cary Eclipse fluorimeter in acetonitrile. Mass spectra were recorded on a Bruker Daltonics MicrOTOF-Q II mass spectrometer under chemical ionization conditions at atmospheric pressure (compounds **2c**,**d**) or electrospray ionization (the rest of the compounds). Elemental analysis was performed on a PerkinElmer PE 2400 series II CHN-analyzer. Melting points were determined with a Boetius apparatus. The TLC analysis was performed on Merck silica gel 60F254 plates, eluent EtOAc, visualization under UV light.

9,10-Phenanthrenequinone (**1**) was purchased from Sigma-Aldrich. 2,7-Dibromo-9,10-phenanthrenequinone (**2a**) [27], 3,6-dibromo-9,10-phenanthrenequinone (**2b**) [31], and pyridine-2-carboxamide hydrazone (**4**) [35] were obtained according to published methods.

2,7-Diiodo-9,10-phenanthrenequinone (2c). *N*-iodosuccinimide (6.48 g, 28.82 mmol) was added to cold (0°C) 98% H_2SO_4 (90 ml), and the mixture was stirred for 25 min at 0°C. Then 9,10-phenanthrenequinone (**1**) (1.50 g, 7.20 mmol) was added, and the mixture was stirred for 24 h at room temperature. The mixture was treated with ice-cold water (200 ml), the precipitate formed was filtered off, washed with water, and dried. The reaction product was used in the next stage without additional purification. Yield 2.94 g (89%), dark-red crystals, mp >250°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.03-8.06 (4H, m, H-3,4,5,6); 8.26 (2H, d, ^4J = 1.2,

H-1,8). Mass spectrum, *m*/*z* (I_{rel}, %): 461 $[M+H]^+$ (100). Found, %: C 36.83; H 1.03. $C_{14}H_6I_2O_2$. Calculated, %: C 36.55; H 1.31.

2-Iodo-9,10-phenanthrenequinone (2d). A mixture of $KMnO_4$ (1.45 g, 9.18 mmol), AcOH (18 ml), Ac_2O (10.5 ml), and I_2 (2.33 g, 9.18 mmol) was cooled to 5°C, and 98% H_2SO_4 (12 ml) was added dropwise at a temperature not exceeding 10°C. Then 9,10-phenanthrenequinone (**1**) (0.83 g, 3.99 mmol) was added and the mixture was stirred for 1 h at 35°C. The reaction mixture was treated with ice-cold water (100 ml) containing previously dissolved Na_2SO_3 and K_2CO_3. The precipitate formed was filtered off, washed with water, and dried. Yield 0.73 g (55%), dark-red crystals, mp 222-224°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.51-7.55 (1H, m); 7.74-7.78 (1H, m); 8.00-8.09 (3H, m); 8.22 (1H, d, ^3J = 8.0, H-4); 8.28 (1H, d, ^4J = 1.6, H 1). Mass spectrum, *m*/*z* (I_{rel}, %): 335 $[M+H]^+$ (100). Found, %: C 50.08; H 2.02. $C_{14}H_7IO_2$. Calculated, %: C 50.33; H 2.11.

Triazatriphenylenes 3a-c, 5a,b (General Method). Amidrazone of pyridine-2-carboxylic acid (**4**) (0.68 g, 5 mmol) was added to a suspension of phenanthrenequinone **2a-d** (5 mmol) in EtOH (500 ml). The mixture was refluxed for 10 h. The reaction mixture was filtered while hot, the obtained precipitate was washed with EtOH and dried. Analytical reference sample was recrystallized from EtOH.

6,11-Dibromo-3-(2-pyridyl)phenanthro[9,10-*e*][1,2,4]triazine (3a). Yield 1.40 g (60%), light-yellow crystals, mp 279-281°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.63-7.67 (1H, m, H-5 Py); 8.07-8.13 (3H, m, H 7,10, H-4 Py); 8.77-8.83 (3H, m, H-8,9, H-3 Py); 8.94 (1H, dd, ^3J = 4.9, ^4J = 1.8, H-6 Py); 9.45 (1H, d, ^4J = 1.8, H-5); 9.51 (1H, d, ^4J = 1.8, H-12). Mass spectrum, *m*/*z* (I_{rel}, %): 467 $[M+H]^+$ (100). Found, %: C 51.22; H 2.01; N 11.73. $C_{20}H_{10}Br_2N_4$. Calculated, %: C 51.53; H 2.16; N 12.02.

7,10-Dibromo-3-(2-pyridyl)phenanthro[9,10-*e*][1,2,4]triazine (3b). Yield 1.49 g (64%), light-yellow crystals, mp >250°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.66-7.70 (1H, m, H-5 Py); 8.08-8.15 (3H, m, H-6,11, H-4 Py); 8.79 (1H, dd, ^3J = 7.5, ^4J = 1.2, H-3 Py); 8.93 (1H, dd, ^3J = 4.9, ^4J = 1.8, H-6 Py); 9.23 (1H, d, ^4J = 1.4, H-8); 9.24 (1H, d, ^4J = 1.4, H-9); 9.27 (1H, d, ^3J = 8.8, H-5); 9.31 (1H, d, ^3J = 8.6, H-12). Mass spectrum, *m*/*z* (I_{rel}, %): 467 $[M+H]^+$ (100). Found, %: C 51.19; H 1.98; N 11.81. $C_{20}H_{10}Br_2N_4$. Calculated, %: C 51.53; H 2.16; N 12.02.

6,11-Diiodo-3-(2-pyridyl)phenanthro[9,10-*e*][1,2,4]triazine (3c). Yield 1.26 g (45%), light-yellow crystals, mp >250°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.66-7.80 (1H, m, H-5 Py); 8.14 (1H, ddd, ^3J = 7.5, ^3J = 7.5, ^4J = 1.8, H-4 Py); 8.25 (1H, dd, ^3J = 8.8, ^4J = 1.7, H-7); 8.30 (1H, dd, ^3J = 8.8, ^4J = 1.7, H-10); 8.61-8.67 (2H, m, H-8,9); 8.79 (1H, dd, ^3J = 7.5, ^4J = 1.2, H-3 Py); 8.95 (1H, dd, ^3J = 4.9, ^4J = 1.8, H-6 Py); 9.59 (1H, d, ^4J = 1.8, H-5); 9.67 (1H, d, ^4J = 1.8, H-12). Mass spectrum, *m*/*z* (I_{rel}, %): 561 $[M+H]^+$ (100). Found, %: C 42.79; H 1.65; N 9.71. $C_{20}H_{10}I_2N_4$. Calculated, %: C 42.89; H 1.80; N 10.00.

A Mixture of 6-Iodo-3-(2-pyridyl)phenanthro[9,10-*e*][1,2,4]triazine (5a) and 11-Iodo-3-(2-pyridyl)phenanthro[9,10-*e*][1,2,4]triazine (5b). Yield 1.19 g (55%), light-yellow crystals. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.61-7.65 (1H, m, H-5 Py); 7.85-8.02 (2H, m); 8.07-8.11 (1H, m, H-4 Py); 8.21 (0.5H, dd, ^3J = 8.4, ^4J = 1.6) and 8.26 (0.5H, dd, ^3J = 8.4, ^4J = 1.6, H-7 (**5a**), H-10 (**5b**)); 8.59 (0.5 H, d, ^3J = 8.4) and 8.62 (0.5H, d, ^3J = 8.4, H-8 (**5a**), H-9 (**5b**)); 8.76-8.82 (2H, m); 8.90 (0.5H, dd, ^3J = 4.9, ^4J = 1.8) and 8.93 (0.5H, dd, ^3J = 4.9, ^4J = 1.8, H-6 Py); 9.39-9.46 (1H, m, H-12 (**5a**), H-5 (**5b**)); 9.65 (0.5H, d, ^4J = 1.6) and 9.73 (0.5H, d, ^4J = 1.6, H-5 (**5a**), H-12 (**5b**)). Mass spectrum, *m*/*z* (I_{rel}, %): 435 $[M+H]^+$ (100). Found, %: C 55.04; H 2.29; N 12.56. $C_{20}H_{11}IN_4$. Calculated, %: C 55.32; H 2.55; N 12.90.

Preparation of Monoazatriphenylenes 6a,b (General Method). A mixture of triazatriphenylene **3a**,**b** (2.50 mmol) and 1-morpholinocyclopentene (2 ml, 12.50 mmol) was stirred under argon atmosphere for 2 h at 200°C, treated with 1-morpholinocyclopentene (1 ml, 6.25 mmol), and stirred for another 1 h under the same conditions. The reaction mixture was cooled to room temperature, and MeCN (30 ml) was added. The obtained mixture was refluxed for 15 min and then maintained for 3 h at room temperature. The precipitate formed was filtered off, washed with MeCN, and dried. Analytical reference sample was obtained by recrystallization from MeCN.

2,7-Dibromo-10-(2-pyridyl)-12,13-dihydro-11*H*-dibenzo[*f*,*h*]cyclopenta[*c*]quinoline (6a). Yield 1.00 g (80%), colorless crystals, mp 242-244°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.22-2.26 (2H, m, 12-CH_2); 3.59-3.63 (4H, m, 11,13-CH_2); 7.34-7.38 (1H, m, H-5 Py); 7.71-7.75 (2H, m, H-3,6); 7.94 (1H, ddd, ^3J = 7.5, ^3J = 7.5, ^4J = 1.8, H-4 Py); 8.28 (1H, d, ^3J = 8.8, H-4); 8.38 (1H, d, ^3J = 8.8, H-5); 8.59 (1H, dd, ^3J = 7.5, ^4J = 1.2, H-3 Py); 8.68 (1H, d, ^4J = 1.8, H-1); 8.75 (1H, dd, ^3J = 4.9, ^4J = 1.8, H-6 Py); 9.49 (1H, d, ^4J = 1.8, H-8). Mass spectrum, *m*/*z* (I_{rel}, %): 505 $[M+H]^+$ (50). Found, %: C 59.44; H 2.97; N 5.50. $C_{25}H_{16}Br_2N_2$. Calculated, %: C 59.55; H 3.20; N 5.56.

3,6-Dibromo-10-(2-pyridyl)-12,13-dihydro-11*H*-dibenzo[*f*,*h*]cyclopenta[*c*]quinoline (6b). Yield 1.03 g (82%), colorless crystals, mp 202-204°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.23-2.27 (2H, m, 12-CH_2); 3.60-3.64 (4H, m, 11,13-CH_2); 7.34-7.38 (1H, m, H-5 Py); 7.74 (1H, dd, ^3J = 8.8, ^4J = 1.6, H-2); 7.79 (1H, dd, ^3J = 8.8, ^4J = 1.6, H-7); 7.92 (1H, ddd, ^3J = 7.5, ^3J = 7.5, ^4J = 1.8, H-4 Py); 8.45 (1H, dd, ^3J = 7.5, ^4J = 1.2, H-3 Py); 8.56-8.62 (2H, m, H-1,4); 8.66 (1H, d, ^4J = 1.6, H-5); 8.75 (1H, dd, ^3J = 4.9, ^4J = 1.8, H-6 Py); 9.30 (1H, d, ^3J = 8.8, H-8). ^{13}C NMR spectrum, δ, ppm: 25.7; 33.3; 37.2; 121.8; 122.1; 123.1 (2C); 123.6; 125.0; 126.0; 127.9; 128.9; 129.0; 130.0; 130.5; 130.7; 130.8; 131.1; 136.4; 139.5; 143.8; 148.6; 150.4; 151.7; 158.4. Mass spectrum, *m*/*z* (I_{rel}, %): 505 $[M+H]^+$ (50). Found, %: C 59.51; H 3.01; N 5.43. $C_{25}H_{16}Br_2N_2$. Calculated, %: C 59.55; H 3.20; N 5.56.

6,11-Diiodo-2-(2-pyridyl)phenanthro[9,10-*b*]pyridine (6c). Triazatriphenylene **3c** (0.5 g, 0.89 mmol) was suspended in 1,2-dichlorobenzene (40 ml). 2,5-Norbornadiene (0.27 ml, 2.67 mmol) was added, and the mixture was refluxed for 35 h while adding 2,5-norbornadiene (0.27 ml, 2.67 mmol) every 8 h. The solvent was removed by distillation under vacuum, the residue was purified by column chromatography (eluent 3:1 CH_2Cl_2–EtOAc, R_f 0.2). Yield 200 mg (40%), light-yellow crystals, mp >250°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.51-7.55 (1H, m, H-5 Py); 8.05-8.09 (3H, m); 8.56-8.60 (2H, m); 8.75-8.79 (3H, m); 9.15 (1H, dd, ^3J = 4.9, ^4J = 1.8, H-6 Py); 9.31 (1H, d, ^3J = 8.8, H-4); 9.70 (1H, d, ^4J = 1.8, H-12). Mass spectrum, *m*/*z* (I_{rel}, %): 559 $[M+H]^+$ (100). Found, %: C 47.01; H 1.93; N 4.87. $C_{22}H_{12}I_2N_2$. Calculated, %: C 47.34; H 2.17; N 5.02.

Preparation of Monoazatriphenylene Aryl Derivatives 7a-d (General Method). A solution of dibromomonoazatriphenylene **6a**,**b** (0.50 mmol) in toluene (25 ml) was treated with the boronic acid **8a**,**b** (1.05 mmol), $PdCl_2(PPh_3)_2$ complex (18 mg, 25 μmol), and PPh_3 (13 mg, 50 μmol). Separately a solution of K_2CO_3 (1.38 g, 10.00 mmol) in distilled water (20 ml) was prepared and added to the reaction mixture. Ethanol (10 ml) was added, and the mixture was stirred under argon atmosphere at 85°C for 7 h. The organic phase was separated, washed with K_2CO_3 and NH_4Cl solutions, then dried over anhydrous Na_2SO_4. The solvents were removed by distillation under vacuum, and the residue was recrystallized from toluene.

2,7-Diphenyl-10-(2-pyridyl)-12,13-dihydro-11*H*-dibenzo[*f*,*h*]cyclopenta[*c*]quinoline (7a). Yield 180 mg (72%), colorless crystals, mp 270-272°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.24-2.28 (2H, m, 12-CH_2); 3.64 (2H, t, ^3J = 7.5, 11-CH_2); 3.78 (2H, t, ^3J = 7.5, 13-CH_2); 7.32-7.36 (1H, m, H-5 Py); 7.41-7.45 (2H, m, H Ph); 7.51-7.57 (4H, m); 7.77-7.81 (2H, m); 7.86-7.97 (5H, m); 8.63 (1H, d, ^3J = 8.8, H-4); 8.65 (1H, dd, ^3J = 7.5, ^4J = 1.2, H-3 Py); 8.72 (1H, d, ^3J = 8.8, H-5); 8.75 (1H, dd, ^3J = 4.9, ^4J = 1.8, H-6 Py); 8.85 (1H, d, ^4J = 1.6, H-1); 9.71 (1H, d, ^4J = 2.0, H-8). ^{13}C NMR spectrum, δ, ppm: 26.0; 33.3; 37.4; 122.7; 122.9; 123.4; 123.6; 123.8; 124.3; 126.0; 126.2; 127.2 (2C); 127.3; 127.4; 128.8; 129.0; 129.6; 130.0; 130.5; 132.1; 132.3; 136.3; 139.1; 139.2; 139.8; 141.1; 141.4; 145.2; 148.4; 150.4; 151.8; 158.9. Mass spectrum, *m*/*z* (I_{rel}, %): 499 $[M+H]^+$ (100). Found, %: C 88.97; H 5.11; N 5.43. $C_{37}H_{26}N_2$. Calculated, %: C 89.13; H 5.26; N 5.62.

2,7-Bis(3,4,5-trimethoxyphenyl)-10-(2-pyridyl)-12,13-dihydro-11*H*-dibenzo[*f*,*h*]cyclopenta[*c*]quinoline (7b). Yield 230 mg (68%), colorless crystals, mp 236-238°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.27-2.31 (2H, m, 12-CH_2); 3.67 (2H, t, ^3J = 7.5, 11-CH_2); 3.82 (2H, t, ^3J = 7.5, 13-CH_2); 3.95 (3H, s, OCH_3); 3.96 (3H, s, OCH_3); 4.01 (6H, s, 2OCH_3); 4.02 (6H, s, 2OCH_3); 6.99 (2H, s, H Ar); 7.08 (2H, s, H Ar); 7.33-7.37 (1H, m, H-5 Py); 7.85-7.96 (3H, m, H-3,6, H-4 Py); 8.65 (1H, d, ^3J = 8.5, H-4); 8.69 (1H, dd, ^3J = 7.5, ^4J = 1.2, H-3 Py); 8.73-8.77 (2H, m, H-5, H-6 Py); 8.85 (1H, d, ^4J = 1.6, H-1); 9.72 (1H, d, ^4J = 2.0, H-8). ^{13}C NMR spectrum, δ, ppm: 26.2; 33.3; 37.4; 53.7; 56.3; 56.4; 61.0; 104.8; 104.9; 123.0; 123.4; 123.5; 123.8; 124.3; 125.3; 126.1; 126.3; 127.3; 129.6; 130.0; 130.5; 132.0; 135.3; 136.3; 137.0; 137.2; 138.0; 138.2; 139.3; 139.4; 140.0; 145.1;

147.6; 148.5; 150.5; 151.9; 153.7; 153.8; 158.7. Mass spectrum, *m*/*z* (I_{rel}, %): 679 $[M+H]^+$ (100). Found, %: C 75.93; H 5.48; N 3.89. $C_{43}H_{38}N_2O_6$. Calculated, %: C 76.09; H 5.64; N 4.13.

3,6-Diphenyl-10-(2-pyridyl)-12,13-dihydro-11*H*-dibenzo[*f*,*h*]cyclopenta[*c*]quinoline (7c). Yield 160 mg (64%), colorless crystals, mp 185-187°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.24-2.28 (2H, m, 12-CH_2); 3.64 (2H, t, ^3J = 7.5, 11-CH_2); 3.73 (2H, t, ^3J = 7.5, 13-CH_2); 7.32-7.36 (1H, m, H-5 Py); 7.42-7.46 (2H, m, H Ph); 7.53-7.57 (4H, m); 7.80-7.84 (4H, m); 7.85-7.97 (3H, m); 8.70 (1H, d, ^3J = 8.2, H-1); 8.75 (1H, dd, ^3J = 4.9, ^4J = 1.8, H-6 Py); 8.82 (1H, d, ^3J = 1.2, H-4); 8.93 (1H, d, ^3J = 1.2, H-5); 9.55 (1H, d, ^3J = 8.5, H-8). ^{13}C NMR spectrum, δ, ppm: 26.0; 33.2; 37.3; 120.9; 121.6; 122.9; 123.7; 125.6; 126.6; 126.7; 127.5 (2C); 127.6; 127.7; 128.2; 128.9; 129.0; 129.4; 130.9; 131.0; 131.3; 136.4; 139.0; 139.6; 141.0; 141.5; 144.7; 148.5; 150.3; 151.8; 158.8. Mass spectrum, *m*/*z* (I_{rel}, %): 499 $[M+H]^+$ (100). Found, %: C 89.00; H 5.13; N 5.39. $C_{37}H_{26}N_2$. Calculated, %: C 89.13; H 5.26; N 5.62.

3,6-Bis(3,4,5-trimethoxyphenyl)-10-(2-pyridyl)-12,13-dihydro-11*H*-dibenzo[*f*,*h*]cyclopenta[*c*]quinoline (7d). Yield 240 mg (71%), colorless crystals, mp 123-125°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.27-2.31 (2H, m, 12-CH_2); 3.66 (2H, t, ^3J = 7.5, 11-CH_2); 3.76 (2H, t, ^3J = 7.5, 13-CH_2); 3.94 (3H, s, OCH_3); 3.95 (3H, s, OCH_3); 3.99 (6H, s, OCH_3); 4.00 (6H, s, OCH_3); 6.98 (2H, s, H Ar); 6.99 (2H, s, H Ar); 7.33-7.37 (1H, m, H-5 Py); 7.86 (1H, dd, ^3J = 8.6, ^4J = 1.8, H-2); 7.89-7.95 (2H, m, H-7, H-4 Py); 8.69 (1H, dd, ^3J = 7.5, ^4J = 1.2, H-3 Py); 8.73 (1H, d, ^3J = 8.6, H-1); 8.74-8.78 (2H, m, H-4, H-6 Py); 8.88 (1H, d, ^4J = 1.8, H-5); 9.57 (1H, d, ^3J = 8.6, H-8). ^{13}C NMR spectrum, δ, ppm: 26.1; 33.2; 37.3; 56.4; 61.1; 104.9; 105.0; 120.7; 121.5; 123.0; 123.1; 123.7; 125.9; 126.8; 126.9; 128.3; 129.4; 130.1; 131.1; 131.2; 136.7; 137.0; 137.5; 138.0; 138.1; 139.1; 140.0; 141.3; 144.8; 148.3; 150.1; 151.9; 153.7; 153.8; 158.4. Mass spectrum, *m*/*z* (I_{rel}, %): 679 $[M+H]^+$ (100). Found, %: C 75.91; H 5.44; N 3.91. $C_{43}H_{38}N_2O_6$. Calculated, %: C 76.09; H 5.64; N 4.13.

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