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The Rh(III)-catalysed C–H/N–H annulation of 2-thienyl- and 2-phenyl-quinazolin-4(3*H*)-ones with diphenylacetylene†

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A series of 4,5-diphenyl-7*H*-thieno[2′,3′:3,4]pyrido[2,1-*b*]quinazolin-7-ones was synthesized *via* the Rh(III)-catalyzed annulation of 2-thienylquinazolin-4(3*H*)-ones with diphenylacetylene. 2-Phenylquinazolin-4(3*H*)-one amide alcoholysis and double C–H functionalization proceeded under the same reaction conditions with the formation of 2,3,7,8-tetraphenyl-1*H*-benzo[*d*,*e*][1,8]-naphthyridine derivatives. All compounds possess fluorescence properties in MeCN and toluene solutions as well as in the solid state. The aggregation induced emission (AIE) properties and the ability to detect Fe^{3+} cations were evaluated.

Introduction

Heteroatom-containing polycyclic compounds with a highly planar structure represent an important class of materials for potential applications in advanced organic electronics. They demonstrate superior photophysical properties as a result of extended π-conjugation, narrow HOMO–LUMO gaps, long wavelength absorption and emission, lower oxidation and/or reduction potentials, strong π–π interactions, and higher mechanical strength.[1–5] Particularly, the rigid π-conjugated heterocyclic systems based on phenanthroimidazole can be used for the creation of organic light emitting diodes (OLEDs) due to strong blue emission. Moreover, a thiophene-fused phenanthroimidazole derivative showed a selective fluorescent response for Fe^{3+}.[6] Polyconjugated systems of dithienoquinazolines and benzo[*f*]thieno[3,2-*h*]quinazolines are considered as prospective materials for organic electronics.[7]

2-Aryl(heteryl)quinazolinones are widely studied heterocyclic compounds, and many studies are being conducted to explore the biological activity of quinazolinone derivatives. However, their molecular framework possesses a strong electron-withdrawing ability and can be used as an acceptor fragment to form push–pull molecules with intramolecular charge transfer (ICT) characteristics. It was shown that 2-[5-(4-diethylaminophenyl)thiophen-2-yl]quinazolin-4(3*H*)-one represents a promising fluorescence molecule with a quantum yield up to 71% in toluene.[8] Applicability of carbazolyl-substituted quinazolinones as hosts for phosphorescent OLEDs has also been explored.[9] Moreover, the quinazolinone structure can serve as a ligand for the construction of complexes. For example, strong emission with high fluorescence quantum yield in solution and in solid state was achieved in asymmetric difluoroboron quinazolinone-pyridine dyes.[10,11] A wide scope of metal complexes of benzazines with possible application as emitters for application in OLEDs has been described as well.[12,13]

Different synthetic approaches for building polycyclic chromophores with π-extended structures are described in the literature.[14–16] For example, the construction of quinazolinone-fused polycyclic frameworks can be reached by annulation of additional rings to parent molecules by transition-metal-catalysed C–H bond functionalization. It is well known that C–H activation represents one of the most attractive approaches due to easy operation, atom- and step-economy, easily available starting materials, high efficiency, and environmental friendliness. Therefore, a large library of C5/C6-benzene-fused isoquinolino[1,2-*b*]quinazolinones was obtained by means of C–H activation.[17–20]

Several methods were devised to modify starting quinazolinones by annulation with alkynes. Some of them include Pd-catalysed aerobic oxidative reactions,[21] one-pot Co(III)-catalysed annulation of 2-aryl(heteryl)quinazolinone-bearing electron-donating and -withdrawing groups,[22] and Ru-catalysed regioselective annulation of 2-styryl and 2-aryl quinazolinones under mild reaction conditions.[23,24] Notably, the synthesis of fused

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heteroarenes can be achieved by $[RuCl_2(p\text{-cymene})]_2$-catalysed aerobic, oxidative dehydrogenation followed by cross-coupling/annulation of dihydroquinazolinones in a one-pot process without purification of intermediates or addition of copper salts.[25] Moreover, Cp*Rh(III) complexes have proved to be highly active catalysts in C–H activation for a vast number of transformations.[6,26–31] Particularly, C6-substituted isoquinolino [1,2-*b*]quinazolines were synthesized *via* Rh(III)-catalysed C–H annulation with sulfoxonium ylides.[30]

Despite the rapid development of chemistry and the biological application of quinazolinone-fused molecules, their photophysical properties have been inadequately investigated. There is great potential for the application of quinazolinone-fused derivatives as photoluminescent materials. It is noteworthy that molecules based on quinazolinone have been shown to be good candidates for organic optical materials such as transistors or bio-probes.[19,32] Moreover, the rotation of phenyl residues can provide the opportunity to realise aggregation-enhanced emission (AEE) or aggregation-induced emission (AIE).

Herein, we report the design, synthesis, and characterization of a series of 4,5-diphenyl-7*H*-thieno[2′,3′:3,4]pyrido[2,1-*b*]quinazolin-7-ones with varying substituents on a thiophen moiety. Readily available thiophenecarboxaldehydes and aminoamides were used as starting materials for the synthesis of key quinazolinone intermediates. The alkyl-substituted thiophenecarboxaldehyde was applied as the starting material to increase the solubility of the target compound. Remarkably, polycyclic compounds based on 2-(thiophen-2-yl)quinazolin-4(3*H*)-ones bearing substituents at the thiophene ring have not yet been described. Additionally, we compared the behaviour of 2-thienyl- and 2-phenyl-quinazolin-4(3*H*)-one under the same reaction conditions. The photophysical properties of the synthesized molecules were investigated in solution and in solid state. We also investigated their AIE characteristics and applicability for the detection of Fe^{3+} cation.

Results and discussion

Synthesis

The quinazolinone core includes two nitrogen atoms ready for C–N bond formation. Therefore, linear and angular annulation may occur, resulting in two regioisomers (Fig. 1). In the synthesis mentioned in the Introduction, cyclisation occurs with regioselective products. In these cases, the N3 atom of quinazolinone participates in the formation of annulated derivatives in a pathway that is more preferable due to the stability of the quinazoline-4(3*H*)-one tautomer.[23] Interestingly, 2-(2-bromophenyl) quinazolin-4(3*H*)-ones in reaction with benzylamines under Cu-catalysed conditions can be converted into two diverse quinazolinone-fused scaffolds, depending on the presence of an oxygen atmosphere.[32]

Cyclization of 2-(2-arylethinylphenyl)-substituted quinazolinone under Fe(III)-catalysed conditions leads to C–N1 annulated products.[33] The same regioisomers were obtained in Ag(I)- or

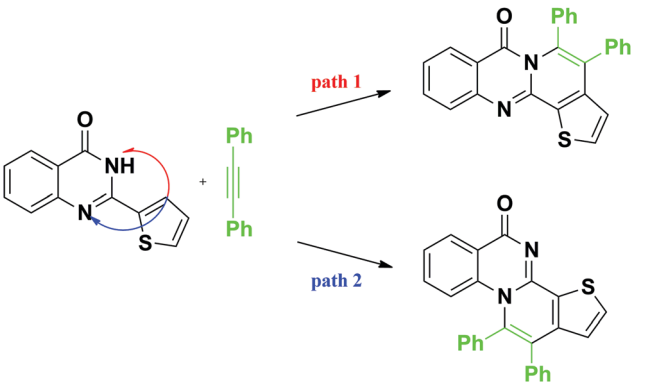


Fig. 1 The cyclisation of 2-(thiophen-2-yl)quinazolin-4-one *via* paths **1** and **2**.

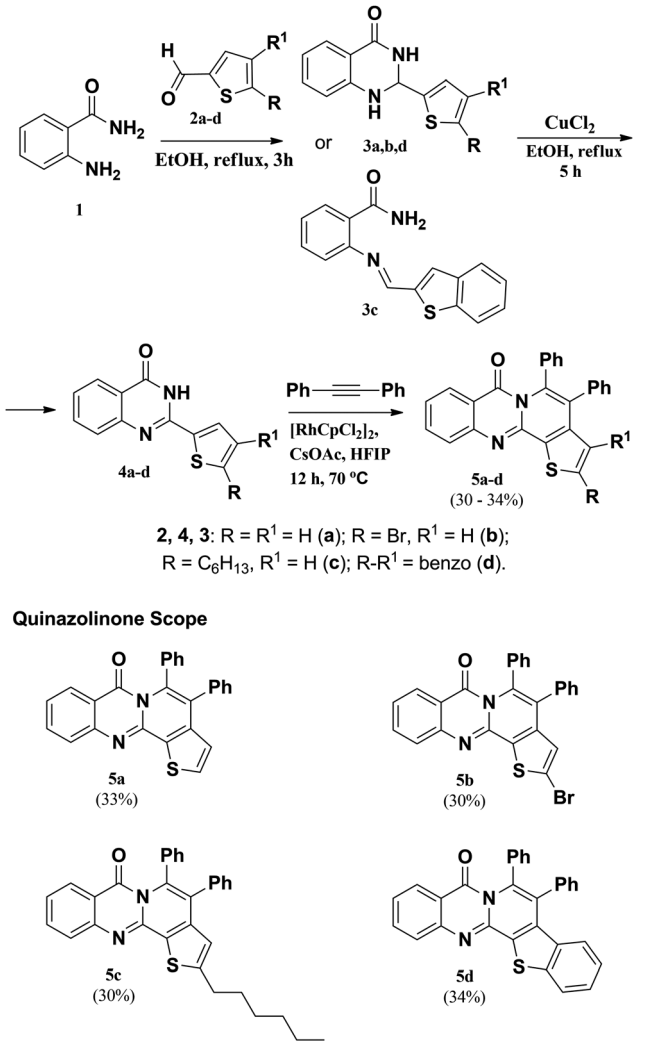
I_2-mediated cascade cyclization of 2-aminobenzamides or anthranilic acids with 2-(phenylethinyl)aldehydes.[34,35] Noteworthy, the cyclometallation process based on 2-thienylquinazoline derivatives proceeds at the C–N1 site.[36,37]

The synthesis of the quinazolinone derivatives **5a–d** is summarised in Scheme 1. The quinazoline-3*H*-ones **4a,b** were obtained as described in previous works.[8,38] For the synthesis of the remaining compounds **4c,d**, a similar procedure was applied. The condensation of anthranilamide **1** with the corresponding 2-thiophencarboxaldehyde **2a–d** and subsequent oxidation with copper(II) chloride led to the 2-(thiophen-2-yl)quinazolin-4(3*H*)-ones **4a–d.**

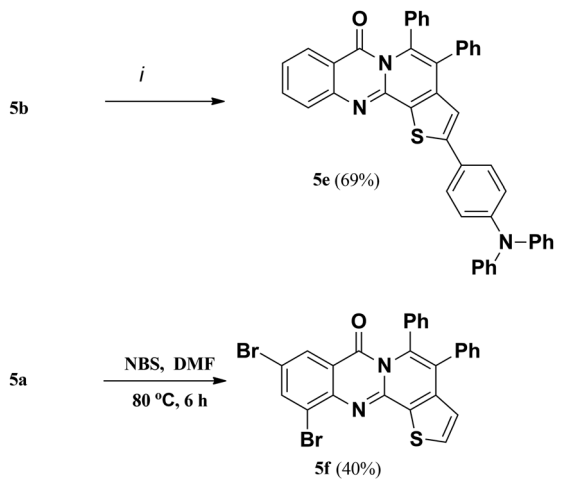
The 2,3-dihydroquinazolin-4(1*H*)-ones **3a,b,d** were isolated as intermediate products, and the presence of signal around 5.9 ppm corresponding to the aliphatic CH group proves the proposed structures (see ESI†). In the case of benzoannulated aldehyde **2c**, Schiff base **3c** was formed, and the signal from the N=CH group at δ 8.95 ppm confirms this fact.

Compounds **5a–d** were obtained according to a previously published procedure.[27] Quinazoline-3*H*-ones **4a–d** were annulated with diphenylacetylene in hexafluoroisopropanol (HFIP) at 70 °C for 12 h using $[RhCp^*Cl_2]_2$ as a catalyst (4 mol%), CsOAc (30 mol%) as a base,[27] and 4,5-diphenyl-7*H*-thieno [2′,3′:3,4]pyrido-[2,1-*b*]quinazolin-7-ones **5a–d** were obtained in moderate yields.

Modification of 4,5-diphenyl-7*H*-(5-bromo)thieno[2′,3′:3,4]pyrido [2,1-*b*]quinazolin-7-one **5b** by a Pd-catalysed cross coupling reaction[39] allowed us to obtain quinazolinone derivative **5e** with an electron-donating diphenylaminophenyl residue at the thiophene ring (Scheme 2, upper line). It is worth noting that an attempt failed to synthesize bromo-derivative **5b** from unsubstituted parent 4, 5-diphenyl-7*H*-thieno[2′,3′:3,4]pyrido[2,1-*b*]quinazolin-7-one **5a** by treatment with *N*-bromosuccinimide (NBS) in DMF at 80 °C for 6 h. It was established that the mentioned conditions led to double bromination at the benzene ring, and 4,5-diphenyl-7*H*-thieno[2′,3′:3,4]pyrido[2,1-*b*]quinazolin-7-one **5f** was isolated as the main product (Scheme 2, bottom line). This result was proven by NMR spectroscopy, as the ^{1}H NMR spectrum of **5f** showed two hydrogen atoms of a benzene ring appearing as two doublets, with a coupling constant of ^4J 2 Hz, while signals from thiophene fragments were



Scheme 1 The synthesis of quinazolinones **5a–d**.



Scheme 2 The synthesis of quinazolinones **5e** and **5f**. i: 4-(diphenylamino)phenylboronic acid, $PdCl_2(PPh_3)_2$, PPh_3, K_2CO_3, toluene, EtOH, and argon, at 85 °C.

located at 6.92 and 7.73 ppm (^3J 5.2 Hz), and their positions were close to those of compound **5a** (see ESI†).

The structures for the remainder of compounds **3–5** were also confirmed by ^{1}H NMR spectroscopy as well as mass-spectrometry and elemental analysis. Additionally, target products **5a–d, f** were characterized by ^{13}C NMR spectroscopy. In the mass spectra of all quinazolinone derivatives **5a–e**, the peaks for molecular ions corresponding to the required [M^+] (404 for compound **5a**, 482 for compound **5b**, 488 for compound **5c**, 454 for compound **5d**, 647 for compound **5e**, and 562 for compound **5e**) were registered. For 4,5-diphenyl-7*H*-thieno-[2′,3′:3,4]pyrido[2,1-*b*]quinazolin-7-one **5a** and **5b**, X-ray single crystal diffraction studies were performed (Fig. 2). According to the XRD data, two independent molecules with similar geometry were crystallized in the centrosymmetric space groups of the triclinic system for compound **5a**.

Due to the stereoeffects of the aryl substituents, the tetracyclic moiety of the molecules is non-planar, and some atoms (as well C7) deviated from the least-squared plane more than 0.3 Å. The deviations from the least-squared plane are 0.75 Å for the O1 atom of the C═O group and more than 0.7 Å for the C22 atom of the aryl substituent. Both aryl substituents are turned on the high angles toward the tetracyclic moiety. Any significantly shortened intermolecular contacts were not observed in the crystal.

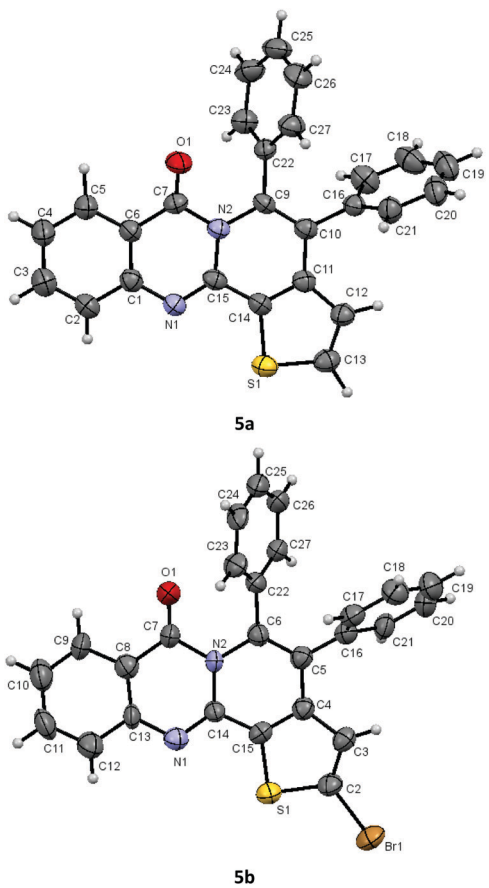


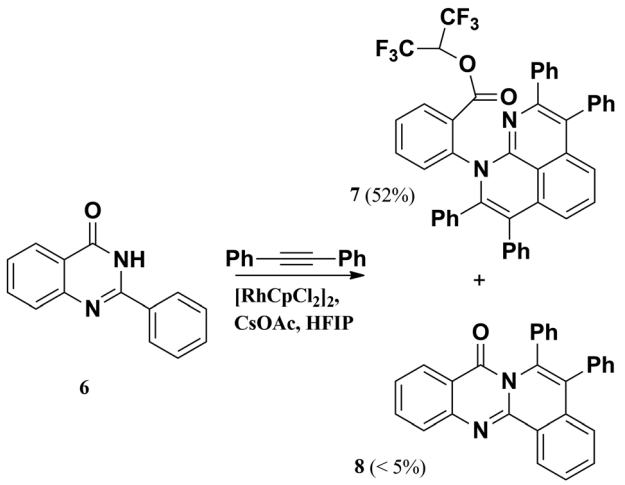
Fig. 2 The molecular structures of **5a** and **5b** using thermal ellipsoids of 50% probability.

Similar to **5a**, two independent molecules of compound **5b** were crystallized in the triclinic system, and the geometry of molecules **5b** was similar to that of **5a**. Compound **5b** was characterized by a distorted polycyclic system and the deviation of the oxygen atom of the carbonyl group from the plane of the heterocycle, as in the case of its counterpart **5a**. Both molecules were organized in dimers in a crystal by means of intermolecular polar contacts between the oxygen of the carbonyl group and the hydrogen of the phenylene fragment of the tetracyclic system as well as due to T-shaped shortened contacts between the Br atom and the phenyl substituent of a neighbouring molecule. The other shortened observed contacts did not lead to a significant deviation from the geometry of non-specific van der Waals interactions.

Bearing in mind that the Ru(II)-catalysed annulation of 2-phenylquinazolinone **6** with diphenylacetylene results in the formation of 5,6-diphenyl-8*H*-isoquinolono[1,2-*b*]quinazolin-8-one,[24] we were interested in the process of quinazolinone **6** undergoing Rh(III)-catalysed annulation (Scheme 3).

Although the same reaction conditions were used as those for the transformation of 2-thienyl counterparts **5a–d**, the desired isoquinolino-quinazolinone **8** was isolated only in trace amounts. The data set indicates that the main product represents the formation of benzonaphthyridine derivative **7** because of amide alcoholysis and the double C–H functionalisation process. Furthermore, the reaction conditions were optimized by the 1 : 2 ratio of starting materials (quinazolinone **6** and diphenylacetylene, respectively), and product **7** was obtained in good yield.

Synthesized compound **7** was characterized by MS, ^{1}H, ^{13}C, and ^{19}F NMR spectral analysis. The relative intensity of the molecular ion peak in the mass spectra of **7** is 75%, and it should be noted that the 100% peak refers to the ion $[M–C(O)OCH(CF_3)_2]^+$. The multiplets in the ^{1}H NMR at δ 6 ppm and in the ^{13}C NMR at δ 67 ppm correspond to the aliphatic CH group, and this result indicates that the HFIP fragments were incorporated into the structure. The presence of two sets of signals



Scheme 3 The formation of the 2,3,7,8-tetraphenyl-1*H*-benzo[*d*,*e*][1,8]-naphthyridine derivative **7**.

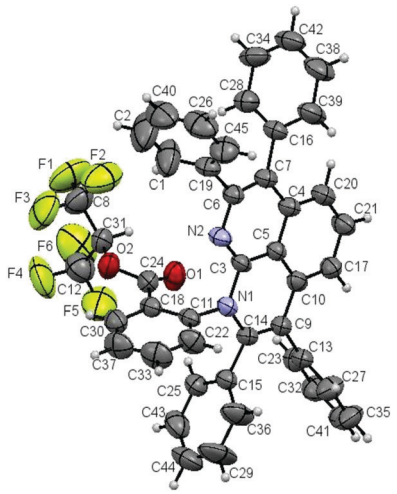


Fig. 3 The molecular structure of **7** using thermal ellipsoids of 50% probability.

in the ^{19}F NMR spectrum related to CF_3 groups provides additional evidence for the formation of the ester moiety. Finally, we were able to confirm the structure of compound **7** by X-ray crystallography (Fig. 3). According to the XRD data, the tricyclic moiety of molecule **7** is planar. The aryl substituents were turned at high angles (60–90°) towards the heterocycle. Any significantly shortened intermolecular contacts in the crystal were not observed.

The difference in the behaviour of 2-thienyl and 2-phenyl quinazolinones (**4**, **6**) can be explained by the electron-donating nature of the thienyl substituent. Therefore, the carbon atom of the C=O group has a weaker electrophilic centre in thienyl derivative **4** than in phenyl derivative **6**. Notably, amide alcoholysis in pyridoquinazolinone coursed by trifluoroethanol has been previously described.[23]

UV/Vis and fluorescence properties

The optical properties of **5a–f**, **7**, and **8** were investigated with UV/Vis and photoluminescence spectroscopy in acetonitrile (MeCN) and toluene solutions at room temperature. The obtained data are summarized in Table 1 and are given in the ESI.†

Quinazolin-7-ones **5a–f**, **7**, **8** were established to show broad long-wave absorption bands in the region of 335–450 nm, which can be attributed to π–π* transitions. The most red-shifted absorption bands were attained with the incorporation of electron-donating amino substituents coupled with the extension of the conjugated π-system (compound **5e**). The presence of alkyl (C_6H_{13}) or halogen (Br) residues in the thiophene ring (**5b**, **5c**) as well as the presence of halogens (Br) in the benzene ring (**5f**) did not significantly affect the shape of the absorption band and was reflected in a redshift of the absorption maximum as compared to **5a**. When proceeding from 4,5-diphenyl-7*H*-thieno[2′,3′:3,4]pyrido[2,1-*b*]quinazolin-7-one (**5a**) to the 5,6-diphenyl-8*H*-isoquinolino[1,2-*b*]quinazolin-8-one (**8**) counterpart, the absorption maximum was bathochromically

Table 1 Optical properties of compounds **5a–f**, **7**, and **8**

Comp.	Solvent	Absorption λ (nm)/ε (10^3 M^{-1} cm^{-1})	Photoluminescence Excitation λ_{max} (nm)	Emission, λ_{max} (nm)	Φ_F,[a] %	Stokes shift, ν_{st} (cm^{-1})
5a	Toluene	383/13.3; 367/12.5; 287/22.7	383, 367, 287	480	<1	5267
	MeCN	378/15.8; 283/29.8	378, 283	480	<1	5622
5b	Toluene	415/9.2; 387/18.1; 374/18.2; 288/36	415, 387, 374, 288	485	1	5221
	MeCN	385/14.8; 284/30.9	385, 284	485	<1	5355
5c	Toluene	385/20.1; 370/18.9; 289/35.2	385, 370, 289	485	1	5355
	MeCN	380/16.7; 285/32.6	380, 285	475	<1	5263
5d	Toluene	419/12.9; 396/20.9; 378/18.9; 337/20; 286/31.9	419, 396, 278, 337, 286	485	2	4634
	MeCN	413/25.9; 391/43.4; 374/38.5; 334/39.3; 275/77.6	413, 391, 374, 334, 275	485	<1	4957
5e	Toluene	423/32.5; 376/35.2; 296/38.9	423, 376, 296	**470**, 500	15	3640
	MeCN	417/19.3; 374/20.7; 291/23.5	417, 374, 291	550	29	5799
5f	Toluene	392/19.7; 296/28.5	392, 296	475	1	4458
	MeCN	386/23.2; 292/35.5	386; 292	470	<1	4630
7	Toluene	433/5.4; 350/22.9	433, 350	560	<1	5238
	MeCN	346/14.2	346	520	<1	8594
	Acetone	434/5.9; 412/6.9; 348/22	—	—	—	—
8	Toluene	392/13.6; 372/19.2; 355/16.8	392, 372, 355	430, **510**	<1	5902
	MeCN	388/12.8; 368/18.3; 351/16.1; 286/37.8	388, 368, 351, 286	430, **510**	<1	6165

[a] Fluorescence quantum yield determined relative to 3-aminophthalimide in ethanol as the standard (Φ_F = 60%).[40] Excitation at 380 nm.

shifted in both solvents. Broad long-wave absorption bands with a maximum at 350 nm (for toluene solution) and 346 nm (for MeCN solution) were observed for benzonaphthyridine derivative **7**.

Compounds **5a–f**, **7**, and **8** exhibited photoluminescent properties (Table S1, ESI†). Depending on the structure and solvent nature, the maxima of the emission bands were in the range of 470–560 nm. The excitation spectra proved to coincide with the absorption spectra. The maxima of fluorescence for **5b**, **5c**, **5d**, and **5e** were redshifted in comparison with unsubstituted **5a** in toluene due to the presence of electron-donating groups in the thiophene fragment. Incorporation of bromines into the benzene portion of quinazolin-7-one led to the opposite effect at 470/475 nm and 480/480 nm (MeCN/toluene solutions) for **5f** and **5a**, respectively. The main emission maximum of phenyl-contained compound **8** (510 nm, in bold) was shifted by 30 nm to the red region in regards to the thiophene-containing analog.

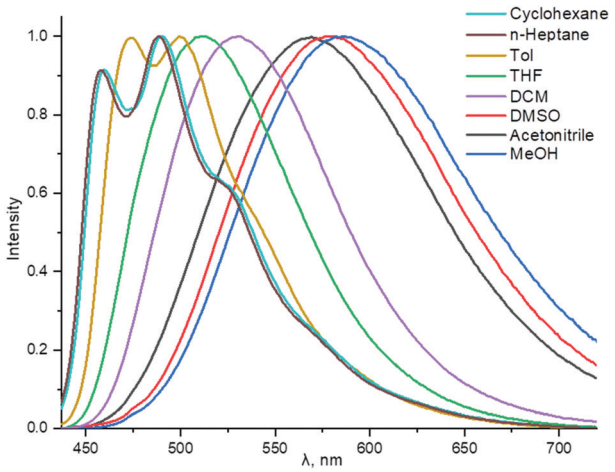


Fig. 4 The normalized emission spectra of **5e** in different solvents.

The solvent effect was different for the obtained compounds. The position of emission maxima for **5a**, **5b**, **5d**, and **8** proved to be independent from their solvent nature. For **5c**, **5f**, and **7**, the solvent effect was expressed as negative solvatochromism, *i.e.*, a hypsochromic shift of fluorescence maxima. For example, the emission maximum was shifted by 10 nm in the blue region upon passing from toluene to acetonitrile for compound **5c**. In the case of benzonaphthyridine derivative **7**, the negative influence of solvent polarity on fluorescence was the strongest (560 nm and 520 nm in toluene and MeCN, respectively). In this case, with the increase in solvent polarity, the ground-state structure of the quinazolin-7-ones became more stabilized than the excited state, because the ground state is more dipolar than the excited state.

The emission band proved to exhibit a bathochromic shift of 80 nm upon increasing the solvent polarity for **5e**. The observed correlation is typical for compounds that undergo an intermolecular photoinduced electron transfer leading to a high polarity state that is stabilized by solvent. Thus, derivative **5e** exhibited satisfactory sensitivity to solvent polarity as well as rather strong fluorescence, and additional emission solvatochromism measurements were obtained for this compound. Diphenylaminophenyl derivative **5e** emits luminescence, from blue in cyclohexane, n-heptane, and toluene to yellow in MeOH. Fig. 4 displays the normalised spectra in various solvents upon UV irradiation of compound **5e**.

The emission quantum yield of considered compounds **5a–d**, **f**, **7**, **8** is rather poor and does not exceed 2%; see Table 1. Only diphenylaminophenyl-substituted quinazolinone **5e** demonstrated moderate quantum yield (15% in toluene and 29% in acetonitrile solution).

Additionally, all compounds **5a–f**, **7**, **8** emitted in solid state (powder), and the emission spectra have been registered and given in the ESI.† According to the obtained data, the emission maxima of quinazolines **5a–f** are located at 493, 506, 476, 501, 508, and 512 nm, respectively (Table S1, ESI†). The emission

maxima for 2-phenylquinazolinone-based molecule **8** appears at 521 nm, naphthyridine derivative **7** demonstrates emission maximum at 568 nm. Redshifts of 8–38 nm observed in emission maxima in the solid state (compounds **5a, b, d–f**, **7**, **8**) compared to toluene solution could be due to the presence of intermolecular interactions existing in the solid state. Hexyl derivative **5c** exhibited an emission that was hypsochromically shifted by 9 nm in the solid state in relation to its toluene solution. It is likely that the hexyl moiety prevents close packaging of the molecules in the solid state.

The fluorescence measurements indicated that the emission intensity of compounds reached 4.2% in the solid state (Table S1, ESI†). In comparison to the solution state, quinazolinones **5a, c, d**, **8** emitted a greater intensity that can be ascribed to restriction of intramolecular motion (RIM) mechanisms. The quantum yields of the bromo-substituted derivatives **5b**, **5f** and compounds **5f**, **7** were less than 1%, and may be attributed to the heavy atom effect or specific intermolecular interactions.

We investigated the aggregation induced emission (AIE) properties[41] of **5a–f**, **7**, **8** and used them as fluorescent probes for Fe^{3+} detection[6] to illustrate their utility. The AIE properties of **5a–d**, **7**, **8** were confirmed by adding water to a series of MeCN solutions (Fig. S29–S34; see the ESI†). The fluorescence spectra of **5a–c**, **8** in the MeCN/H_2O mixtures with various water fractions (f_w) are presented at an excitation wavelength of 378–390 nm. As an example, the spectrum of quinazolinone **5c** in a MeCN/water mixture with different water fractions is shown in Fig. 5. Quinazolin-7-ones **5a–d**, **8** showed one weak fluorescence peak in pure MeCN. The spectral characteristics of **5a–d**, **8** showed no significant change on average for f_w in the range from 0% to 70%. When the water fraction increased to more than 70%, the fluorescence strength significantly increased due to the formation of the aggregation state of **5a–d**, **8**. The enhanced fluorescence intensity may be due to the change in the aggregate morphology. In the case of **7**, at first, it is observed quenching fluorescence at f_w = 10%, and then, fluorescence is absent in the range of 10–60% (f_w). The aggregation state of **7** is formed at f_w > 60%. In addition, the fluorescence emission of **7** in the aggregated state is redshifted compared with pure MeCN, 540 and 490 nm.

The ability of compounds **5a–d, f**, **7** to sense Fe^{3+} was investigated. For this reason, the emission spectrum in pure acetone solution was registered. There was a 100-fold enhancement of the fluorescence intensity of an acetone solution of **7** after the addition of Fe^{3+}, as shown in Fig. 6(a). In addition, the fluorescence change was detected under a UV lamp by the naked eye (Fig. 6(b), inset).

Fe^{3+} probably coordinates with the C=O groups and nitrogen atoms of **7**, and therefore, the structural rigidity is enhanced and the π-electron distribution changes. The formation of Fe^{3+} complexes by means of lone pairs of electrons for the nitrogen and carbonyl groups has been previously demonstrated.[42,43] No changes were observed in the fluorescence emission spectra of a solution of **7** by adding other metal ions, namely Cu^{2+} and Cr^{3+}, which are two of the most common interferents for Fe^{3+} detection (Fig. 6(b)).[44] Adding Fe^{3+} into solutions of **5a–d, f** resulted in fluorescence quenching that may be due to Fe^{3+} behaving like a Lewis acid (see the ESI† and Fig. S35–S39).

Experimental

Methods

Unless otherwise indicated, all common reagents and solvents were used from commercial suppliers without further purification. Melting points were measured on a Boetius instrument. Thin-layer chromatography (TLC) and column chromatography were carried out on SiO_2. The ^1H NMR (400 Hz), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz) spectra were obtained on a Bruker Avance II DMX400 spectrometer using $CDCl_3$ or

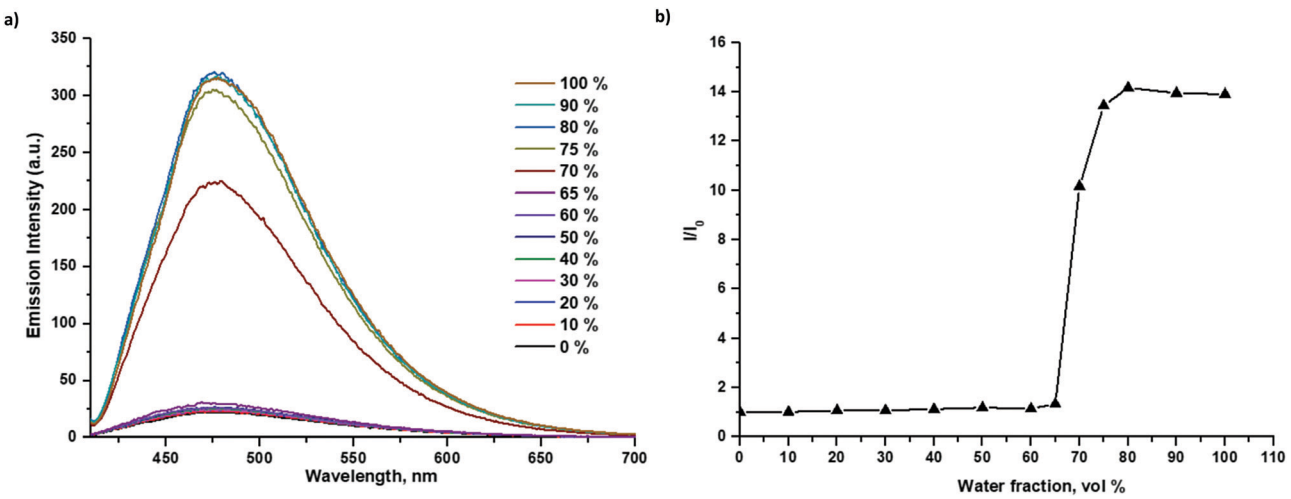


Fig. 5 (a) The fluorescence spectra of 10 μM **5c** in MeCN/H_2O mixtures with different water fractions (f_w). (b) A plot of I/I_0 at 475 nm *versus* the composition of the MeCN/H_2O mixture for **5c** (E_{ex} = 385 nm).

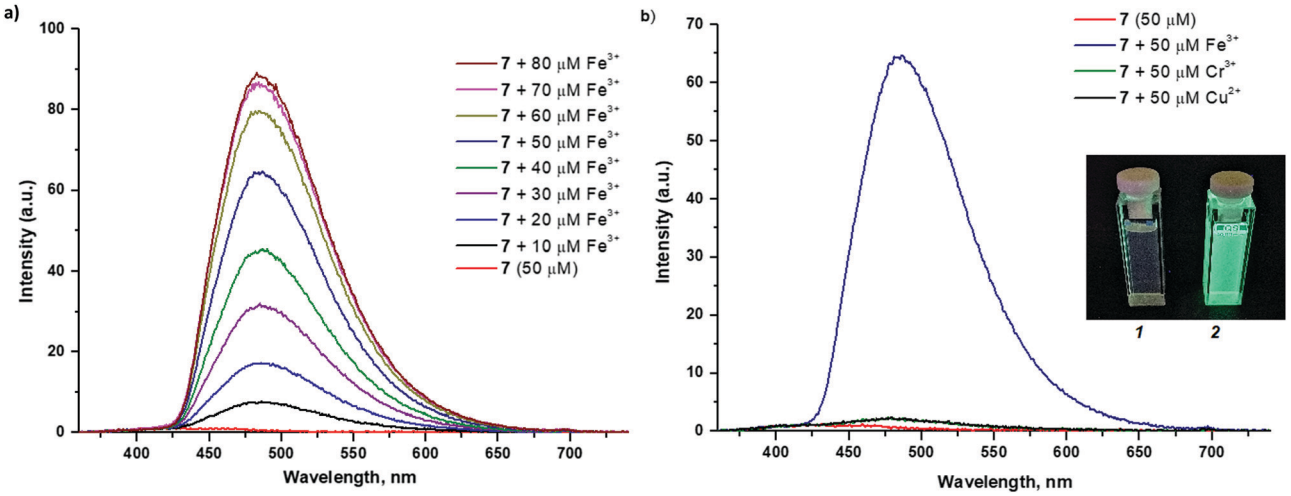


Fig. 6 Selective Fe^{3+} detection using **7**: (a) fluorescence emission spectra (λ_{ex} = 350 nm) of an acetone solution of **7** with different concentrations of Fe^{3+} (10–70 μM). (b) Fluorescence emission spectra (λ_{ex} = 350 nm) for an acetone solution of **7** (50 μM) with Cu^{2+} and Cr^{3+} (50 μM). Inset: A photo of acetone solutions of **7** without (1) or with (2) Fe^{3+} under a UV lamp (λ_{ex} = 365 nm).

DMSO-d_6 as the solvent. The ^{1}H NMR spectra of compound 7 were recorded at room temperature at 600 MHz on a Bruker DRX-600 spectrometer. The ^{19}F NMR spectra were recorded with $CFCl_3$ (C_6F_6 was used as a secondary reference, δ_F – 162.9 ppm). Mass spectra were recorded on a Shimadzu GCMS-QP2010 Ultra instrument with electron ionization (EI) of the sample. Elemental analysis (C, H, N) was performed using a PerkinElmer 2400 elemental analyser. UV/Vis spectra were recorded for 1×10^{-5} M solutions with a Shimadzu UV-2600 spectrophotometer. Photoluminescent spectra were recorded for 1×10^{-6} M solutions on a Varian Cary Eclipse fluorescence spectrophotometer. The emission spectra in different solvents were recorded using a Horiba FluoroMax-4. UV/Vis and fluorescence spectra were recorded using standard 1 cm quartz cells at room temperature. Fluorescence spectra in the solid state were measured using an integrating sphere Quanta-ϕ F-3029 with a Horiba FluoroMax-4 spectrofluorometer.

For Fe^{3+} detection, test solutions containing 50 μM **5a–f** and 7 and 10x μM Fe^{3+} (x = 1, 2, 3, 4, 5, 6, 7) were prepared by adding 100x μL $FeCl_3{\cdot}6H_2O$ acetone solution (0.4 mM) and (2000–100x) μL acetone to 2 mL of 7 acetone solution (0.1 mM). Solutions containing other metal ions (Cu^{2+} and Cr^{3+}) were prepared using $Cu(NO_3)_2{\cdot}6H_2O$ and $CrCl_3{\cdot}6H_2O$ instead of $FeCl_3{\cdot}6H_2O$. Compound **5e** did not dissolve in acetone.

Crystallography

Single crystal XRD experiments were performed for an orange block (0.47 × 0.31 × 0.11 mm) of compound **5a**, yellow prism (0.45 × 0.35 × 0.25 mm) of compound **5b**, and yellow prism (0.44 × 0.36 × 0.27 mm) of compound 7 on an Xcalibur 3 automated diffractometer using a standard procedure (graphite-monochromated Mo Kα-irradiation, T = 295(2) K, ω-scanning with 1° steps). An empirical absorption correction was applied. Using Olex2,[45] the structures were solved with the ShelXS structure solution program using Direct Method and refined with the ShelXL[46] refinement package using full-matrix Least Squares minimization. All non-hydrogen atoms were refined using an anisotropic approximation; H-atoms were placed in the calculated positions and isotropically refined in the "rider" model.

Crystal data for 5a. $C_{26}H_{16}N_2OS$, M = 404.47, triclinic, a = 8.9557(7) Å, b = 9.9486(8) Å, c = 22.5422(17) Å, α = 98.812(6)°, β = 91.216(9)°, γ = 97.590(6)°, V = 1965.6(3) Å^3, space group $P\bar{1}$, Z = 4, μ(Mo Kα) = 0.186 mm^{-1}. On the angles $3.50 < \theta < 31.01$, 17 949 reflections measured, 10 435 unique (R_{int} = 0.0644), which were used in all calculations. Goodness to fit at F^2 1.001. The final wR_2 = 0.2254 (all data) and R_1 = 0.0740 ($I > 2\sigma(I)$). Largest diff. peak and hole 0.366 and −0.364 ē Å^{-3}.

Crystal data for 5b. $C_{26}H_{15}BrN_2OS$, M = 483.37, triclinic, a = 12.3877(11) Å, b = 13.2907(12) Å, c = 14.7438(13) Å, α = 105.626(8)°, β = 107.407(8)°, γ = 103.726(8)°, V = 2092.9(3) Å^3, space group $P\bar{1}$, Z = 4, μ(Mo Kα) = 2.085 mm^{-1}. On the angles $3.64 < \theta < 28.28$, 21 802 reflections measured, 10 261 unique (R_{int} = 0.0747), which were used in all calculations. Goodness to fit at F^2 0.982. The final wR_2 = 0.1862 (all data) and R_1 = 0.0624 ($I > 2\sigma(I)$). Largest diff. peak and hole 0.644 and −0.648 ē Å^{-3}.

Crystal data for 7. $C_{45}H_{28}F_6N_2O_2$, M = 742.69, triclinic, a = 10.8731(13) Å, b = 12.7566(16) Å, c = 14.5064(19) Å, α = 66.069(12)°, β = 86.317(10)°, γ = 85.015(10)°, V = 1831.2(4) Å^3, space group $P\bar{1}$, Z = 2, μ(Mo Kα) = 0.104 mm^{-1}. On the angles $3.50 < \theta < 26.37$, 12 984 reflections measured, 7267 unique (R_{int} = 0.0732), which were used in all calculations. Goodness to fit at F^2 1.001. The final wR_2 = 0.1826 (all data) and R_1 = 0.0718 ($I > 2\sigma(I)$). Largest diff. peak and hole 0.200 and −0.268 ē Å^{-3}.

The results of the X-ray diffraction analysis for compounds **5a**, **5b**, and 7 were deposited with the Cambridge Crystallographic Data Centre (CCDC 2004850, 2004711, and 1999651, respectively).†

Synthetic procedures

Preparation of intermediates. The quinazoline-4(*3H*)-ones **4a,b** were obtained from 2-aminobenzamide **1** and the

appropriate thiophen-2-carboxaldehyde **2** in two steps using previously developed methods.[8,38] The compounds **4c,d** were synthesized using a similar procedure.

2-(5-Hexylthiophen-2-yl)-2,3-dihydroquinazolin-4(1*H*)-one (3c). A solution of 2-aminobenzamide **1** (0.50 g, 3.7 mmol) in ethanol (20 mL) and 5-hexylthiophen-2-carboxaldehyde **2c** (0.72 g, 3.7 mmol) was refluxed for 3 h. The mixture was cooled, and the solvent was evaporated. The product was washed with EtOH (5 mL) to obtain a pale yellow solid, yield 82%, m.p. 165–167 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$), δ: 0.88 (3H, m, CH_3), 1.30 (6H, m, $2CH_2$), 1.59 (2H, m, CH_2), 2.72 (2H, t, ^3J = 7.5 Hz, CH_2), 5.89 (1H, s, 2-H), 6.61 (1H, m, 4′-H), 6.67 (1H, m, benzo), 6.73 (1H, d, ^3J = 7.7 Hz, benzo), 6.88 (1H, d, ^3J = 3.9 Hz, 3′-H), 7.05 (1H, br s, NH), 7.21 (1H, m, benzo), 7.60 (1H, d, ^3J = 7.6 Hz, benzo), 8.20 (1H, br s, NH). MS (*m*/*z*, I_{rel}%): 315 $[M + 1]^+$ (17), 314 $[M]^+$ (63), 313 $[M - H]^+$ (100), 281 (30), 229 (11), 147 (48), 121 (12), 120 (95), 119 (18), 97 (30), 92 (30), 65 (10); molecular formula $C_{18}H_{22}N_2OS$; requires $[M]^+$ 314. Elemental analysis: found C, 68.73; H, 7.08; N, 8.89%; requires C, 68.75; H, 7.05; N, 8.91%.

2-((Benzo[*b*]thiophen-2-ylmethylene)amino)benzamide (**3d**) was synthesized using a procedure similar to that used for **3c**. After cooling, the precipitate was filtered and washed with MeCN to obtain a colourless solid, yield 91%, m.p. 204–206 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$), δ: 7.31 (1H, d, ^3J = 8.1 Hz), 7.35 (1H, m), 7.42–7.50 (2H, m), 7.54 (1H, m), 7.60 (1H, br s, NH_2), 7.98 (2H, m), 8.09 (2H, m), 8.38 (1H, br s, NH_2), 8.95 (1H, s, N=CH). MS (*m*/*z*, I_{rel}%): 281 $[M + 1]^+$ (18), 280 $[M]^+$ (79), 279 $[M - H]^+$ (74), 247 (12), 160 (11), 147 (54), 146 (21), 134 (54), 121 (11), 120 (100), 119 (35), 92 (52), 91 (11), 65 (21), 64 (12), 63 (13); molecular formula $C_{16}H_{12}N_2OS$; requires $[M]^+$ 280. Elemental analysis: found C, 68.58; H, 4.33; N, 9.97%; requires C, 68.55; H, 4.31; N, 9.99%.

2-(5-Hexylthiophen-2-yl)quinazoline-4(3*H*)-one (4c). 2-(5-Hexylthiophen-2-yl)-2,3-dihydroquinazolin-4(1*H*)-one **3c** (0.94 g, 3.0 mmol) was dissolved in ethanol (20 mL), $CuCl_2$ (0.54 g, 4 mmol) was added, and the reaction mixture was refluxed for 5 h. After cooling, the formed quinazolinone **4c** was filtered and washed with EtOH (3 mL) and hexane (3 mL) to obtain a pale yellow solid, yield 80%, m.p. 175–177 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$), δ: 0.90 (3H, m, CH_3), 1.32–1.40 (6H, m, $2CH_2$), 1.69 (2H, m, CH_2), 2.84 (2H, t, ^3J = 7.5 Hz, CH_2), 6.85 (1H, d, ^3J = 3.9 Hz, 4′-H), 7.41 (1H, m, 7-H), 7.57 (1H, d, ^3J = 7.7 Hz, 5-H), 7.74 (1H, m, 6-H), 8.01 (1H, d, ^3J = 3.9 Hz, 3′-H), 8.09 (1H, d, ^3J = 8.2 Hz, 8-H), 12.44 (1H, s, NH). MS (*m*/*z*, I_{rel}%): 313 $[M + 1]^+$ (14), 312 $[M]^+$ (65), 242 (25), 241 $[M - C_5H_{11}]^+$ (100); molecular formula $C_{18}H_{20}N_2OS$; requires $[M]^+$ 312. Elemental analysis: found C, 69.18; H, 6.47; N, 8.92%; requires C, 69.20; H, 6.45; N, 8.97%.

2-(Benzo[*b*]thiophen-2-yl)quinazoline-4(3*H*)-one (**4d**) was synthesized using a method similar to that used to obtain **4c** in MeOH, with refluxing for 11 h. Colourless solid, yield 50%, m.p. > 300 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$), δ: 7.43–7.48 (3H, m, 7-H, 5′-H, 6′-H), 7.69 (1H, d, ^3J = 8.2 Hz, 5-H), 7.79 (1H, m, 6-H), 7.91 (1H, dd, ^3J = 6.7 Hz, ^4J = 1.4 Hz, 4′-H or 7′-H), 7.95 (1H, d, ^3J = 7.4 Hz, 4′-H, 7′-H), 8.15 (1H, dd, ^3J = 7.9 Hz, ^4J = 1.3 Hz, 8-H), 8.54 (1H, s, 3′-H), 12.80 (1H, br s, NH). MS (*m*/*z*, I_{rel}%): 279 $[M + 1]^+$ (20), 278 $[M]^+$ (84), 159 (13), 150 (27), 133 (10), 120 (11), 119 (64), 105 (18), 104 (51), 103 (14), 92 (26), 91 (100), 90 (21), 89 (29), 79 (10), 78 (17), 79 (23), 51 (21), 50 (12), 45 (74), 43 (80), 42 (15), 39 (20); molecular formula $C_{16}H_{10}N_2OS$; requires $[M]^+$ 278. Elemental analysis: found C, 69.06; H, 3.60; N, 10.03%; requires C, 69.04; H, 3.62; N, 10.06%.

Starting 2-phenyl-3*H*-quinazolin-4-one **6** was obtained by treatment of anthranilamide with benzoyl chloride as previously described.[47]

General procedure for the synthesis of compounds 5a–d

The synthesis of products **5a–d** was accomplished using a protocol similar to a previously published procedure.[27] To a suspension of corresponding 2-(thiophen-2-yl)quinazoline-4(3*H*)-one **4a–d** (0.90 mmol) in HFIP (3 mL), diphenylacetylene (0.19 g, 1.08 mmol), $[RhCp^*Cl_2]_2$ (22 mg, 36 μmol), and CsOAc (0.05 g, 0.27 mmol) were added. The mixture was stirred at 70 °C for 12 h in a round-bottom pressure flask.

4,5-Diphenyl-7*H*-thieno[2′,3′:3,4]pyrido[2,1-*b*]quinazolin-7-one (**5a**) was synthesized following a general procedure. The reaction mixture was cooled, and acetone (2 mL) was added. The formed precipitate was filtered and washed with acetone (1 mL) and hexane (1 mL). Yellow solid, yield 33%, m.p. 262–264 °C (lit. m.p. 250–251 °C).[22] ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.90 (1H, d, ^3J = 5.2 Hz, 3-H), 7.08 (4H, m, Ph), 7.16 (3H, m, Ph), 7.23 (3H, m, Ph), 7.36 (1H, m, 10-H), 7.66 (1H, d, ^3J = 5.2 Hz, 2-H), 7.79 (2H, m, 8-H, 9-H), 8.17 (1H, d, ^3J = 8.0 Hz, 11-H). ^{13}C NMR (100 MHz, DMSO-d$_6$), δ: 118.8, 124.8, 124.9, 124.9, 125.7, 126.6, 126.7, 126.8, 127.2, 127.9, 128.8, 130.1, 131.9, 134.7, 134.7, 135.6, 136.0, 136.3, 141.8, 144.8, 146.8, 160.2. MS (*m*/*z*, I_{rel}%): 405 $[M + 1]^+$ (31), 404 $[M]^+$ (100), 403 (30), 375 (12); molecular formula $C_{26}H_{16}N_2OS$; requires $[M]^+$ 404. Elemental analysis: found C, 77.18; H, 4.02; N, 6.92%; requires C, 77.20; H, 3.99; N, 6.93%.

The reagents were stirred in HFIP (5 mL) for 14 h following a general procedure. After cooling, the precipitate was filtered and washed with acetone (1 mL) and hexane (1 mL). The product was extracted with $CHCl_3$ and purified by column chromatography on SiO_2, with the eluent gradually changing from hexane to hexane/EtOAc (1/1). Yellow solid, yield 30%, m.p. 265–266 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.86 (1H, s, 3-H), 7.03–7.08 (4H, m, Ph), 7.16–7.18 (3H, m, Ph), 7.25 (3H, m, Ph), 7.34–7.38 (1H, m, 10-H), 7.77 (2H, m, 8H, 9-H), 8.15 (1H, d, ^3J = 8.0 Hz, 11-H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 119.5, 121.9, 124.7, 125.2, 126.2, 127.4, 127.6, 127.7, 128.3, 128.3, 128.8, 130.4, 133.9, 134.8, 135.6, 136.2, 137.1, 142.2, 144.1, 147.5, 161.1. MS (*m*/*z*, I_{rel}%): 485 $[M + 3]^+$ (29), 484 $[M + 2]^+$ (100), 483 $[M + 1]^+$ (50), 482 $[M]^+$ (95), 481 (22), 201 (29), 194 (16); molecular formula $C_{26}H_{15}BrN_2OS$; requires $[M]^+$ 482. Elemental analysis: found C, 77.18; H, 4.02; N, 6.92%; requires C, 64.60; H, 3.13; N, 5.80%.

4,5-Diphenyl-7*H*-(5-hexyl)thieno[2′,3′:3,4]pyrido[2,1-*b*]quinazolin-7-one (**5c**) was synthesized following a general procedure. The reaction mixture was cooled and partially evaporated, acetone (2 mL) was added, and the formed precipitate was filtered and washed with acetone (1 mL) and hexane (1 mL).

The product was purified by column chromatography on SiO_2, with the eluent gradually changing from hexane to hexane/EtOAc (1/1). Pale yellow solid, yield 30%, m.p. 150–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.88 (3H, t, ^3J = 6.1 Hz, CH_3), 1.30 (4H, m, $2CH_2$), 1.38 (2H, m, CH_2), 1.72 (2H, m, CH_2), 2.87 (2H, t, ^3J = 7.6 Hz, CH_2), 6.57 (1H, s, 3-H), 7.06 (4H, m, Ph), 7.16 (3H, m, Ph), 7.23 (3H, m, Ph), 7.33 (1H, m, 10-H), 7.76 (2H, m, 8-H, 9-H), 8.15 (1H, d, J = 8.01 Hz, 11-H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 14.2, 22.6, 28.9, 31.1, 31.5, 31.6, 119.2, 122.5, 124.6, 125.6, 126.1, 127.2, 127.3, 127.4, 127.6, 128.1, 128.9, 130.5, 130.9, 134.6, 136.2, 136.4, 136.7, 142.5, 145.2, 147.8, 154.9, 161.4. MS (*m/z*, I_{rel}%): 490 $[M + 2]^+$ (11), 489 $[M + 1]^+$ (36), 488 $[M]^+$ (100), 417 $[M - C_5H_{11}]^+$ (15); 43 (13); molecular formula $C_{32}H_{28}N_2OS$; requires $[M]^+$ 488. Elemental analysis: found C, 78.63; H, 5.80; N, 5.72%; requires C, 78.66; H, 5.78; N, 5.73%.

6,7-Diphenyl-8*H*-benzo[4′,5′]thieno[2′,3′:3,4]pyrido[2,1-*b*]quinazolin-8-one (5d). 6,7-Diphenyl-8*H*-benzo[4′,5′]thieno[2′,3′:3,4]pyrido[2,1-*b*]quinazolin-8-one (**5d**) was synthesized following a general procedure. After cooling, the precipitate was filtered and washed with acetone (1 mL) and hexane (1 mL). The product was purified by column chromatography on SiO_2, with the eluent gradually changing from hexane to hexane/EtOAc (4/1). Yellow solid, yield 34%, m.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.49 (1H, d, ^3J = 8.3 Hz,), 7.06 (1H, m), 7.15–7.20 (7H, m, Ph), 7.31–7.35 (3H, m), 7.35–7.42 (2H, m), 7.80 (1H, m, 10-H), 7.86 (1H, d, ^3J = 8.0 Hz, 9-H), 7.95 (1H, d, ^3J = 8.0 Hz), 8.19 (1H, d, ^3J = 8.0 Hz, 12-H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 119.4, 123.2, 124.9, 125.3, 125.5, 126.2, 126.5, 127.2, 127.4, 127.7, 128.1, 128.5, 129.0, 131.0, 134.8, 135.8, 135.9, 136.0, 136.7, 137.5, 142.9, 145.2, 147.7, 161.0. MS (*m/z*, I_{rel}%): 456 $[M + 2]^+$ (11), 455 $[M + 1]^+$ (36), 454 $[M]^+$ (100), 453 (15), 227 (12); molecular formula $C_{30}H_{18}N_2OS$; requires $[M]^+$ 454. Elemental analysis: found C, 79.25; H, 3.97; N, 6.14%; requires C, 79.27; H, 3.99; N, 6.16%.

4,5-Diphenyl-7*H*-(5-(4-diphenylaminophenyl))thieno[2′,3′:3,4]-pyrido[2,1-*b*]quinazolin-7-one (5e). 4,5-Diphenyl-7*H*-(5-(4-diphenylaminophenyl))thieno[2′,3′:3,4]-pyrido[2,1-*b*]quinazolin-7-one (**5e**) was synthesized using a protocol similar to a previously published procedure.[39] To a suspension of 4,5-diphenyl-7*H*-(5-bromo)thieno[2′,3′:3,4]pyrido[2,1-*b*]quinazolin-7-one **5b** (0,10 g, 0.21 mmol) in toluene (10 mL), 4-(diphenylamino)phenylboronic acid (0.07 g, 0.25 mmol), $PdCl_2(PPh_3)_2$ (15 mg, 0.02 mmol), PPh_3 (10 mg, 0.04 mmol), solution of K_2CO_3 (0.2 g, 1.4 mmol) in water (1.2 mL), and EtOH (1.2 mL) were added. The mixture was stirred at 85 °C for 14 hours under an argon atmosphere in a round-bottom pressure flask. After cooling the mixture, EtOAc/water (1/1, 10 mL) was added. The organic layer was separated, and the aqueous layer was extracted with additional EtOAc (2 × 10 mL). The combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The product was purified by column chromatography on SiO_2, gradually changing from hexane to hexane/EtOAc (1/9). Yellow solid, yield 69%, m.p. > 280 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.93 (1H, s, 3-H), 7.03–7.17 (16H, m), 7.26 (3H, m), 7.28–7.33 (4H, m), 7.50 (2H, d, ^3J = 7.9 Hz), 7.78 (2H, m, 8-H, 9-H), 8.16 (1H, d, ^3J = 8.0 Hz, 11-H). MS (*m/z*, I_{rel}%): 649 $[M + 2]^+$ (18), 648 $[M + 1]^+$ (54), 647 $[M]^+$ (100), 485 (10), 484 (38), 483 (18), 482 (33), 404 (29), 324 (34), 201 (13), 57 (12); molecular formula $C_{44}H_{29}N_3OS$; requires $[M]^+$ 647. Elemental analysis: found C, 81.56; H, 4.54; N, 6.47%; requires C, 81.58; H, 4.51; N, 6.49%.

4,5-Diphenyl-9,11-dibromo-7*H*-benzo[*b*]thieno[2′,3′:3,4]pyrido-[2,1-*b*]quinazolin-7-one (5f). To a suspension of **5a** (0.12 g, 0.3 mmol) in DMF (3 mL), a solution of NBS (0.127 g, 0.72 mmol) in DMF (2 mL) was added. The mixture was stirred at 80 °C for 6 h. After cooling and partial evaporation, water (3 mL) was added. The formed precipitate was filtered off and washed with hexane (2 mL). The product was purified by column chromatography on SiO_2, with hexane/EtOAc eluent (5/1). Yellow solid, yield 40%, m.p. = 249–251 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.92 (1H, d, ^3J = 5.3 Hz, 3-H), 7.06 (4H, m, Ph), 7.16 (3H, m, Ph), 7.25 (3H, m, Ph), 7.73 (1H, d, ^3J = 5.3 Hz, 2-H), 8.15 (1H, d, ^4J = 2.0 Hz), 8.25 (1H, d, ^4J = 2.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 117.1, 121.1, 122.0, 125.7, 126.6, 127.5, 127.6, 127.7, 128.2, 128.9, 129.5, 130.3, 133.1, 134.2, 135.6, 135.9, 136.4, 140.4, 142.8, 144.2, 145.7, 159.8. MS (*m/z*, I_{rel}%): 565 $[M + 5]^+$ (16), 564 $[M + 4]^+$ (57), 563 $[M + 3]^+$ (35), 562 $[M + 2]^+$ (100), 561 $[M + 1]^+$ (27), 560 $[M]^+$ (50), 484 (19), 483 (13), 482 (19), 374 (20), 373 (23), 372 (24), 281 (11), 186 (14), 77 (13); molecular formula $C_{26}H_{14}Br_2N_2OS$; requires $[M]^+$ 560. Elemental analysis: found C, 55.52; H, 2.54; N, 4.95%; requires C, 55.54; H, 2.51; N, 4.98%.

1,1,1,3,3,3-Hexafluoropronan-2-yl-2-(2,3,7,8-tetraphenyl-1*H*-benzo[*d*,*e*][1,8]-naphthyridin-1-yl)benzoate (7) was synthesized following a previously published procedure.[27] To a suspension of 2-(phen-2-yl)quinazoline-4(3*H*)-one **6** (0.9 mmol) in HFIP (6 mL), diphenylacetylene (0.39 g, 2.16 mmol), $[RhCp^*Cl_2]_2$ (45 mg, 72 μmol), and CsOAc (0.1 g, 0.54 mmol) were added. The mixture was stirred at 70 °C for 12 h in a round-bottom pressure flask. The reaction mixture was cooled, and acetone (2 mL) was added. The formed precipitate was then filtered off and washed with acetone (1 mL) and hexane (1 mL). The product was purified by column chromatography on SiO_2, with CH_2Cl_2 eluent. Yellow solid, yield 52%, m.p. 218–220 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 6.01 (1H, m, $CH(CF_3)_2$), 6.60 (1H, d, ^3J = 7.4 Hz), 6.88–7.05 (13H, m), 7.12–7.26 (5H, m), 7.27–7.32 (5H, m), 7.39 (1H, m), 7.43 (1H, m), 8.01 (1H, dd, ^3J = 8.0 Hz, ^4J = 1.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 66.90 (m, $CH(CF_3)_2$), 116.3, 118.6, 119.6, 120.2, 122.3, 125.5, 126.6, 126.8, 126.9, 127.0, 127.6, 127.7, 127.8, 128.0, 128.0, 128.3, 128.9, 130.3, 131.3, 131.5, 131.6, 131.8, 132.8, 134.9, 135.2, 136.6, 137.1, 138.9, 139.5, 140.9, 141.3, 141.7, 149.1, 152.6, 162.6. ^{19}F NMR (376 MHz, $CDCl_3$), δ: −73.15 (m), −72.73 (m). MS (*m/z*, I_{rel}%): 744 $[M + 2]^+$ (20), 743 $[M + 1]^+$ (55), 742 $[M]^+$ (75), 741 (10), 549 (19), 548 (63), 547 (100) $[M - C(O)OCH(CF_3)_2]^+$, 546 (12), 469 (10), 371 (11), 287 (11), 273 (17), 272 (10), 265 (14), 264 (11), 234 (14), 233 (11), 77 (10); molecular formula $C_{45}H_{28}F_6N_2O_2$; requires $[M]^+$ 742. Elemental analysis: found C, 79.25; H, 3.97; N, 6.14%; requires C, 72.77; H, 3.80; N, 3.77%.

5,6-Diphenyl-8*H*-isoquinolino[1,2-*b*]quinazolin-8-one (8). Pale yellow solid, yield <5%, m.p. 240–242 °C (lit. m.p. 249–250 °C).[22] ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.08–7.13 (7H, m, Ph), 7.19 (1H, d, ^3J = 7.7 Hz, 4-H), 7.27 (3H, m, Ph), 7.41 (1H, m, 11-H), 7.57 (1H, m 2-H or 3-H), 7.64 (1H, m, 2-H or 3-H), 7.82 (1H, m, 10-H), 7.89 (1H, m, 9-H), 8.17 (1H, d, ^3J = 7.9 Hz, 12-H), 9.13 (1H, d, ^3J = 7.9 Hz, 1-H). MS (*m/z*, I_{rel}%): 399 $[M + 1]^+$ (31), 398 $[M]^+$

(100), 397 (38), 381 (11), 369 (14); molecular formula $C_{28}H_{18}N_2O$; requires $[M]^+$ 398. Elemental analysis: found C, 84.38; H, 4.57; N, 7.01%; requires C, 84.40; H, 4.55; N, 7.03%.

Conclusions

We have successfully applied the mild Rh(III)-catalysed annulation of 2-thienylquinazolinone with diphenylacetylene for the synthesis of 4,5-diphenyl-7*H*-thieno[2′,3′:3,4]pyrido[2,1-*b*]quinazolin-7-ones. Interestingly, under the same reaction conditions, 2-phenylquinazolinone undergoes a transformation into the 2,3,7,8-tetraphenyl-1*H*-benzo[*d*,*e*][1,8]-naphthyridine derivative. Luminescence in solution as well as in the solid state, aggregation-induced emission, and the sensing abilities of the considered polycyclic compounds were investigated. The quinazolinone with a diphenylaminophenyl substituent at the thiophene ring demonstrated the highest luminescence intensity in MeCN solution (29%). Some of the derivatives were shown to sense Fe^{3+} cations.

Author contributions

Tatyana N. Moshkina: investigation; Emiliya V. Nosova: project administration; Galina N. Lipunova: conceptualization; Ekaterina F. Zhilina: methodology; Pavel A. Slepukhin: validation; Igor L. Nikonov: data curation; Valery N. Charushin: supervision.

Conflicts of interest

There are no conflicts to declare.

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