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Synthesis and photophysical studies of novel 4-aryl substituted 2-phenyl-, 2-(fluoren-2-yl)- and 2-cymantrenylquinazolines

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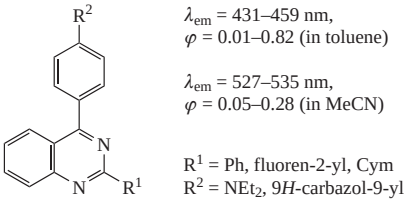
The synthesis of novel push–pull 2,4-disubstituted quinazolines was performed by the bromodeoxygenation of 2-phenyl-, 2-(fluoren-2-yl)- and 2-cymantrenylquinazolin-4-ones and subsequent palladium-catalyzed Suzuki reactions. According to the optical studies, derivatives containing 4-positioned 4-diethylaminophenyl substituent exhibit higher luminescence in toluene solutions as compared to acetonitrile ones.

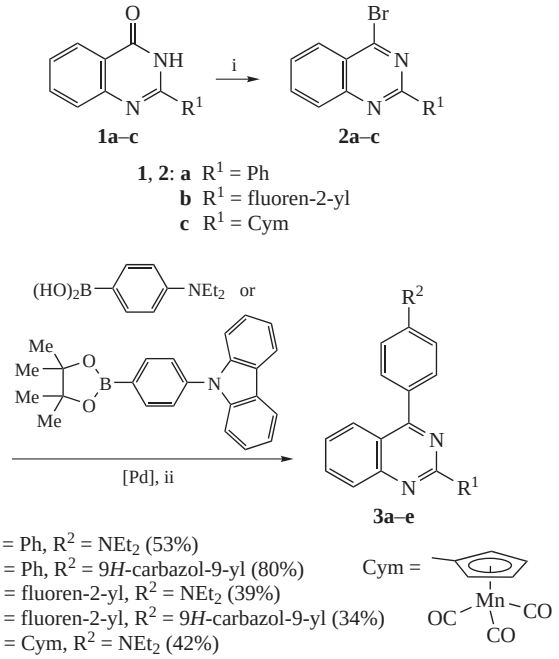


2,4-Disubstituted quinazolines bearing aryl groups represent promising probes with tunable fluorescent properties and electron buffering material for electroluminescent devices.[1–4] 2,4-Bis(arylalkynyl)-, 2-aryl-4-arylalkynyl- and 2-(4-diethylaminophenyl)-4-aryl-containing quinazolines gained recognition due to their potential in pH sensing.[1,2] Amino substituted arylvinylquinazolines demonstrated strong emission solvatochromism and colour change upon addition of acid, so these push–pull systems are prospective for nonlinear optical (NLO) studies and for colorimetric pH sensors.[3] Recently, we reported the synthesis of novel push–pull 2-(thiophen-2-yl)-4-(morpholin-4-yl)quinazolines bearing electron donating fragment in thiophene ring and possessing solvatochromic and acidochromic properties.[5] Some of 2,4-disubstituted quinazolines can be used for the synthesis of cyclometalated complexes with luminescent properties.[6,7]

The aim of this work was the synthesis of new 2,4-diarylated quinazolines **3a–e** of donor–acceptor type with 2-phenylquinazoline, 2-(fluoren-2-yl)quinazoline or 2-cymantrenylquinazoline moieties as electron acceptor unit. All these compounds bear electron donating substituent at the 4-position of quinazoline.

Replacement of 2-positioned phenyl group with fluorenyl one leads to considerable extending of π-conjugated system. Incorporation of electron withdrawing and bulky cymantrenyl fragment instead of phenyl one at the 2-position of quinazoline seems to be an original approach for tuning optical properties of molecules.[8] Data on luminescent properties of cymantrenyl-substituted (het)arenes are scarce.[9–12] It is of note that position of cymantrenyl residue is crucial for luminescent properties, and incorporation of cymantrenylvinyl residue instead of styryl one into *trans*-2-(2-phenylethenyl)-3-phenyl-3*H*-quinazolin-4-one leads to luminescence quenching.[12]

Synthesis of the target quinazolines **3a–e** is outlined in Scheme 1.[†] 2-Phenylquinazolin-4-one **1a** was obtained by treatment of anthranilamide with benzoyl chloride as described.[13] Quinazolinone **1b** was synthesized for the first time from anthranilamide and fluorene-2-carbaldehyde and subsequent oxidative cyclization of the intermediate azomethine similar to the method reported earlier.[14] 2-Cymantrenylquinazolin-4-one **1c** was obtained from formylcymantrene and anthranilamide in



Scheme 1 *Reagents and conditions*: i, $POBr_3$, NEt_3, PhMe, 80 °C, 12 h; ii, arylboronic reactant, $PdCl_2(PPh_3)_2$, PPh_3, K_2CO_3, PhMe, EtOH, 85 °C, 7 h.

[†] For the detailed synthetic procedures, see Online Supplementary Materials.

two steps, the corresponding Schiff base was transformed into quinazolinone **1c** by refluxing in ethanol with copper(II) chloride. Compounds **1a**–**c** were converted into 4-bromo derivatives **2a**–**c** upon treatment with $POBr_3$ in toluene in the presence of triethylamine.[15] Further, bromides **2a**–**c** were introduced into the Pd-catalyzed Suzuki cross-coupling reaction with 4-diethylaminophenylboronic acid or 4-(9*H*-carbazol-9-yl)phenylboronic acid pinacol ester with 34–80% yields (for procedures, see refs. 5, 16). Notably, 4-bromo-2-phenylquinazoline did not undergo substitution reaction with *N*,*N*-dialkylanilines as C-nucleophiles.

The structures of quinazolines **3a**–**e** were confirmed by ^{1}H and ^{13}C NMR and mass spectra. The ^{1}H NMR spectrum of **3e** is characterized by two signals of cyclopentadienyl residue at 5–6 ppm, their location is similar to that of other cymantrenyl derivatives.[9] The signal of cymantrenyl CO carbons in ^{13}C NMR spectra of compound **3e** was observed at 224.83 ppm. In the mass spectra of carbazolylphenylquinazolines **3b**,**d**, peaks of molecular ions with 100% intensity were detected, whereas the mass spectra of diethylaminophenylated quinazolines **3a**,**c** revealed $[M-Me]^+$ peak with 100% intensity; mass spectra of 2-cymantrenylquinazoline **3e** were characterized by $[M-3CO]^+$ peak with 100% intensity.

According to the XRD data, three independent molecules of compound **3b** with nearest geometrical parameters are crystallized in the chiral space group of the triclinic system (Figure 1).‡ For all molecules, the quinazoline and carbazole moieties are placed approximately in the same plane. The turning angle between the plane of the phenylene bridge and the plane of the heterocycle is 51(1)°. No any shortened intermolecular contacts in the crystal were observed.

The photophysical properties of 2,4-disubstituted quinazolines **3a**–**e** were evaluated in two solvents with different dielectric constants, namely toluene (ε_r = 2.38) and acetonitrile (ε_r = 36.64).[18] The spectral data are summarized in Table 1 and the UV-VIS spectra are presented in Online Supplementary Materials. All compounds (except for **3b**) demonstrate absorption wavelengths at λ_{max} = 391–405 and 285–322 nm, and clear solvatochromism was not observed. However, the ratio of band intensities changes depending on the solvent polarity, and, to a greater degree, on the nature of the 2-positioned substituent (see Online Supplementary Materials). Note that the long-wave band is caused by electron transfer from the electron donating 4-positioned substituent towards the quinazoline fragment.

Compounds **3a**–**c**,**e** proved to possess fluorescence depending on solvent. For acetonitrile solutions, the maxima of the emission bands are located at 527–535 nm, whereas toluene solutions demonstrated luminescence at 431–459 nm (see Table 1). Therefore, red shift of emission bands occurs with increase in solvent polarity (Figure 2).

The Stokes shifts are rather large, thus providing a clear indication of a high polarizability of the π-conjugated systems. It is established that donor–acceptor functionalized molecules can lead to ICT processes, and this phenomenon explains the large Stokes shifts. It should be noted that the values of Stokes shifts considerably grow upon transition from toluene to acetonitrile solutions (see Table 1). This may be due to greater stabilization of the polarized molecules **3a**–**e** in the excited state by more polar molecules of a solvent.

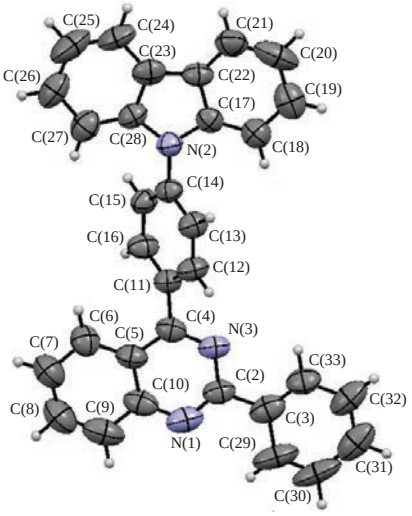


Figure 1 Molecular structure of compound **3b** in the thermal ellipsoids of 50% probability.

Table 1 Optical spectroscopy data for the quinazoline derivatives **3a**–**e**.

Compound	Solvent	λ_{abs}/nm[a]	λ_{em}/nm	φ (%)[b]	Stokes shift $\Delta\nu_{St}$/cm^{-1}
3a	MeCN	263, 393	530	28	6577
	toluene	285, 391	448	82	3254
3b	MeCN	238, 259, 291, 339	527	26[c]	10532
	toluene	293, 341	431	<1	6124
3c	MeCN	242, 275, 325, 394	531	21	6548
	toluene	330, 392	459	61	3723
3d	MeCN	237, 290, 322, 405	–	–	–
3e	MeCN	255, 395	535	5	6625
	toluene	312, 387	446	38	3418

[a] Room temperature, c = 0.1 μmol ml^{-1}. [b] 3-Aminophthalimide in ethanol as standard (φ = 60%), excitation at 400 nm.[19] [c] Quinine sulfate in 0.1 M H_2SO_4 as standard (φ = 54%), excitation at 350 nm.[20]

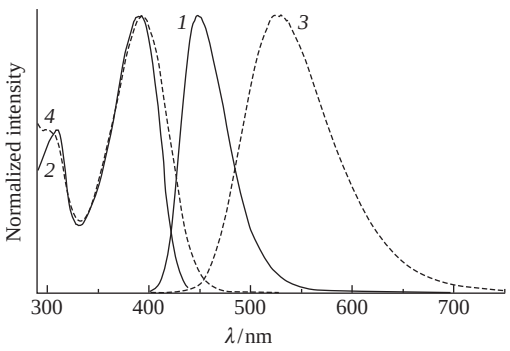


Figure 2 (*1*, *3*) Normalized emission and (*2*, *4*) fluorescence excitation spectra of quinazoline **3a** in (*1*, *2*) toluene and (*3*, *4*) acetonitrile.

‡ The single crystal (light yellow prism, 0.25 × 0.2 × 0.15 mm) of compound **3b** ($C_{32}H_{21}N_3$) was used for X-ray analysis. Analysis was performed at 295(2) K on an Xcalibur 3 diffractometer using graphite monochromated CuKα irradiation (λ = 1.54184 Å) and CCD detector. An empirical absorption correction was applied (μ = 0.542 mm^{-1}). Crystal is triclinic, space group *P*1, a = 9.008(6), b = 9.415(9) and c = 22.97(2) Å, α = 85.33(7)°, β = 86.14(6)°, γ = 76.88(6)°, V = 1889(3) Å^3, Z = 3. On the angles 3.87° < θ < 67.11° total of 21883 reflections were measured, among them 6459 unique reflections (R_{int} = 0.0435), 4491 reflections with $I \geqslant 2\sigma(I)$. Completeness to θ = 67.1088° was 95.52%. The structure was solved by direct method and refined by full-matrix least squares at F^2 using the SHELXTL program package.[17] All non-hydrogen atoms were refined anisotropically, the positions of the hydrogen atoms were calculated as a riding model in isotropic approximation. Goodness to fit at F^2 was 1.0188; final R values [$I > 2\sigma(I)$]: R_1 = 0.0505, wR_2 = 0.1292; R values (all reflections): R_1 = 0.0633, wR_2 = 0.1339. Largest difference peak and hole were 0.1943 and –0.2300 e Å^{-3}.

CCDC 1547817 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Fluorescence quantum yields of quinazolines **3a–e** are strongly dependent on the polarity of solvents and the structure of compounds. Thus, 4-diethylaminophenyl derivatives **3a**,**c**,**e** exhibited higher luminescence in toluene solutions as compared with acetonitrile ones. Incorporation of more bulky fluorenyl fragment into the 2-position of quinazoline (compound **3c**) led to the decrease in luminescence quantum yield compared to 2-phenyl counterpart **3a**. A sharp decrease in the emission intensity was observed when diethylamino group was replaced with carbazolyl one (compound **3b**); moreover, such a substitution accomplished along with the incorporation of fluorenyl fragment resulted in the complete luminescence quenching (compound **3d**). Such an influence of the carbazolylphenyl residue may be caused by destruction of the conjugation resulted from the withdrawal of the phenylene fragment from the quinazoline plane. Incorporation of bulky cymantrenyl group into the molecule (**3e**) led to considerable decrease in luminescence intensity both in acetonitrile and toluene solutions.

In summary, novel 4-(4-diethylaminophenyl)- and 4-[4-(9*H*-carbazol-9-yl)phenyl]quinazolines **3a–e** have been synthesized starting from the corresponding 2-substituted quinazolin-4-ones. For diethylaminophenyl derivatives **3a**,**c**,**e**, more intensive blue luminescence in toluene solutions compared to orange luminescence in acetonitrile has been demonstrated. The molecule of **3e** is the first example of the structure in which cymantrenyl residue is directly bonded with quinazoline core.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.01.010.

References

1 S. Achelle, J. Rodriguez-López and F. Robin-le Guen, *J. Org. Chem*., 2014, **79**, 7564.
2 M. J. Mphahlele, H. K. Paumo, A. M. El-Nahas and M. M. El-Hendawy, *Molecules*, 2014, **19**, 795.
3 S. Achelle, A. Barsella, C. Baudequin, B. Caro and F. R. Guen, *J. Org. Chem*., 2012, **77**, 4087.
4 Z. Zhang, J. Xie, H. Wang, B. Shen, J. Zhang, J. Hao, J. Cao and Z. Wang, *Dyes Pigments*, 2016, **125**, 299.
5 E. V. Nosova, T. N. Moshkina, G. N. Lipunova, D. S. Kopchuk, P. A. Slepukhin, I. V. Baklanova and V. N. Charushin, *Eur. J. Org. Chem*., 2016, **2016**, 2876.
6 Q. Mei, L. Wang, Y. Guo, J. Weng, F. Yan, B. Tian and B. Tong, *J. Mater. Chem*., 2012, **22**, 6878.
7 E. V. Nosova, T. N. Moshkina, D. S. Kopchuk, G. N. Lipunova, P. A. Slepukhin and V. N. Charushin, *Mendeleev Commun*., 2016, **26**, 129.
8 K. F. McDaniel, in *Comprehensive Organometallic Chemistry II*, eds. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Oxford, 1995, vol. 6, pp. 93–107.
9 M. Hromadová, M. Salmain, R. Sokolová, L. Pospíšil and G. Jaouen, *J. Organomet. Chem*., 2003, **668**, 17.
10 K. Lam and W. E. Geiger, *J. Organomet. Chem*., 2016, **817**, 15.
11 H. T. Poh, J. W. Kee, T. S. Chwee and W. Y. Fan, *J. Organomet. Chem*., 2014, **759**, 11.
12 E. S. Kelbysheva, L. N. Telegina, E. A. Ershova, T. V. Strelkova, M. G. Ezernitskaya, E. V. Nosova, F. F. Smol'yakov, F. M. Dolgushin and N. N. Loim, *Russ. Chem. Bull., Int. Ed*., 2017, **66**, 327 (*Izv. Akad. Nauk, Ser. Khim*., 2017, 327).
13 A. A. Layeva, E. V. Nosova, G. N. Lipunova, T. V. Trashakhova and V. N. Charushin, *Russ. Chem. Bull., Int. Ed*., 2007, **56**, 1821 (*Izv. Akad. Nauk, Ser. Khim*., 2007, 1758).
14 E. V. Nosova, T. N. Moshkina, G. N. Lipunova, I. V. Baklanova, P. A. Slepukhin and V. N. Charushin, *J. Fluorine Chem*., 2015, **175**, 145.
15 W. N. Harnish and A. A. Ramsey, *Patent US 3998951 A*, 1976.
16 D. S. Kopchuk, A. F. Khasanov, I. S. Kovalev, G. V. Zyryanov, G. A. Kim, I. L. Nikonov, V. L. Rusinov and O. N. Chupakhin, *Chem. Heterocycl. Compd*., 2014, **50**, 871 (*Khim. Geterotsikl. Soedin*., 2014, 943).
17 G. M. Sheldrick, *Acta Crystallogr*., 2008, **A64**, 112.
18 Y. Ooyama, Y. Oda, T. Mizumo and J. Ohshita, *Tetrahedron*, 2013, **69**, 1755.
19 N. A. Borisevich, V. V. Zelinskii and B. S. Neporent, *Dokl. Akad. Nauk SSSR*, 1954, **94**, 37 (in Russian).
20 W. H. Melhuish, *J. Phys. Chem*., 1961, **65**, 229.

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