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New *meso* substituted cyanine dyes in the 2-R-5H-[1,2,4]triazolo[5,1-a] isoindole series

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Abstract

meso-Substituted symmetrical monomethine cyanine dyes derived from the triazoloisoindole were obtained by reaction of 2-R-5H-[1,2,4]triazolo[5,1-a]isoindoles with acyl chlorides. The *meso* group can be varied in a wide range enhancing the interest of these dyes like biological probes. Spectral UV–vis properties are reported.

Keywords: Triazoloisoindole; Cyanine dyes; Acylation reactions; Synthesis; UV–vis

1. Introduction

While the chemistry of simple isoindoles is well-studied [1–5], a little is known about fused isoindoles containing a nodal nitrogen atom, in particular, triazoloisoindoles presented here. These compounds are not explored systematically [6] despite of their importance for heterocyclic chemistry as synthetic intermediates, as well as their particular biological and physical properties [7–16]. In synthesis, only one reaction of alkylation, cyanoethylation, by interaction with isocyanates and isothiacyanates, and a reaction of acylation for two compounds are described [17,18].

To the best of our knowledge, apart from our previous work [19], no *meso* substituted mono or trimethine derivatives are known in the triazolo or tetrazoloisoindole series.

Thus, following our recent results the present report deals with a new synthetic method of the *meso*-substituted monomethinecyanines in the triazoloisoindole row. This allows introduction of different alkyl, aryl and heteroaryl substituents at the methine group.

2. Results and discussion

The aim of our work is the systematic investigation of the reaction of acyl derivatives with triazoloisoindoles. In this area, we are mainly interested about the possibility to form monomethinecyanine dyes under the acylation reaction conditions as it was the case with tetrazolo[5,1-a]isoindole [18].

In the triazolo series, only one acyl derivative **I** is reported [16,17], obtained from 2-phenyl-1-methyl-5H-[1,2,4]triazolo [5,1-a]isoindole **II** perchlorate by action of acetic acid anhydride in DMF (Scheme 1).

The choice of the triazoloisoindole is due to the fact that owing to reactivity indexes, triazoloisoindole must be one of the most active azoloisoindoles [20]; moreover, this system also enables a variation of the substitutions in two sites of the triazole ring.

To introduce a wide range of R substituents (see Table 1), we used the more available acyl chlorides instead of carboxylic acid anhydrides, and we began to utilize the related quaternary salt **II** instead of the hard-to-reach and unstable triazoloisoindole **III**. We tried multiple conditions for the acylation by varying the solvent and reactants (dioxane + K_2CO_3, dioxane + Et_3N, pyridine), but in most cases the new cyanine dyes **IV** were formed (Scheme 2).

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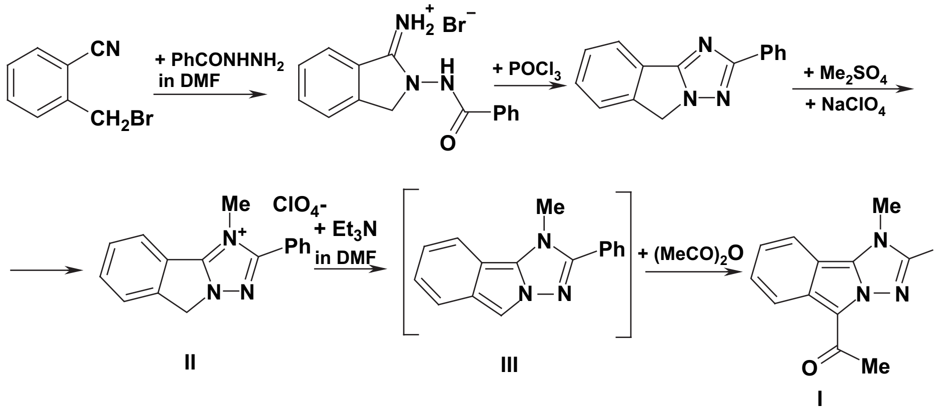


Scheme 1. Synthesis of acyl derivative **I**.

We observed that the ease to isolate the final products depends on the ratios of starting materials and some regularity can be disclosed. At a molar ratio [starting salt:acyl chloride:-triethylamine, 1:1:1], the dye is formed in interesting amount, but some unreacted salt remains impeding the separation of **IV**; in the case of the ratio 2:1:1 less quantity of dye is formed and much unreacted salt remains; at mixing ratio 1:1:3 or 2:1:3 significant oily residues are observed. Thus, the ratio 1:1:2 seems preferable. Easy dye isolation also depends on the nature of the anion; the best results were obtained for the perchlorate salts.

The nature of R also influences the reaction. The isolation of the acylated product **I** was successful only for **Ia** (R = 4-Br-phenyl; R^1 = Me; R^2 = 4-Br-phenyl) and **Ib** (R = 2-furyl; R^1 = Me; R^2 = Et). In the other cases, dyes **IVc**, **d** were obtained with significant yields. If R is aromatic or heteroaromatic, the yield of cyanine dyes increases, mainly with the presence of a para electron-donor substituent. But in this case it is difficult to isolate the acylated products. Quaternary salts **II** with R = 1-naphthyl, 5-NO_2-furan, 5-Br-furan lead to resin formation, which hinders the isolation of final products. Acyl chlorides with electron-acceptor substituents significantly decreases the yield of dyes **IVf**, **p**.

All separated products were characterized by the usual physicochemical methods (see Section 4) but we will emphasize hereafter some UV–vis properties (Table 1).

At each λ_{max} is associated a hypsochromic shoulder between 34.5 and 47.5 nm (Table 1). Following the literature [21] this fact may be related to aggregates or vibrational and rotational additional transitions. To try to understand the nature of these bands, we made some dilution experiments with products **IVc**, **d** and **g** in ethanol, acetonitrile and methylene chloride. In all cases except one, the Beer–Lambert law was strictly respected (Fig. 1). The deconvolution of the experimental curves shows that the two band surfaces ratio is constant and near from 10/90. We found only one exception with compound **IVd** in acetonitrile. In this case, we observed a nonlinear variation of the peak surfaces ratio, mainly due to the shoulder one. In our concentration range ($5.26-0.5\times 10^{-5}\ \mathrm{M\,l^{-1}}$) the ratio varied from 15/85 to 10/90. This effect may be due to the presence of the R^2 anisyl group but this assumption is not supported by any previous result.

Thus the aggregates hardly can be the reason for the dissymmetry in the charge distribution and therefore for the shoulder which is insensitive to solvent dilution [22].

Finally, we observed for all the **IV** compounds only moderate solvatochromic effects, i.e. the bathochromic shifts referred to acetonitrile are always lower than 4 nm with toluene and methylene chloride. The only noticeable fact is the presence of an important new band for **IVd** in toluene (Do = 0.45, λ = 520 nm) as compared to the λ_{max} band (Do = 0.4, λ = 584 nm) which may be the indication of a specific interaction (perhaps an aromatic π–π stacking between the ending heterocycles and the toluene).

3. Conclusion

Finally, we propose a new, simple and efficient method for the synthesis of *meso*-substituted cyanine dyes **IV**, with a large range of substituents R^2. We will take advantage of this to introduce functional groups for the grafting with products of biological interest or to enhance their solubility in water. This work also demonstrates the ability of another type of azoloisoindole to react with acyl chlorides giving previously unreachable dyes.

4. Experimental

4.1. General methods

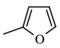
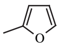
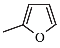
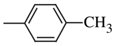
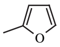
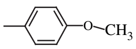
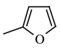
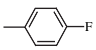
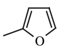
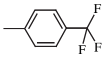
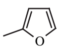
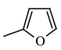
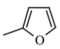
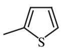
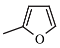
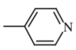
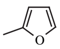
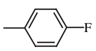
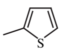
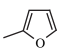
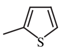
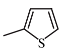
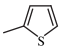
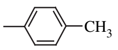
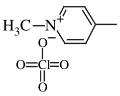
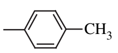
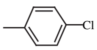
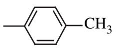
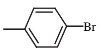
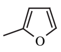
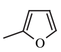
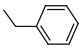
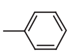
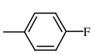
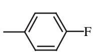
The ^1H and ^{13}C NMR spectra (400 and 100 MHz) were recorded with a Varian Mercury 400 with TMS as an internal standard.

The UV–vis spectra were recorded on a Perkin–Elmer Lambda-19 spectrophotometer equipped with a 60 mm integration sphere for solid measurements; the deconvolution of the spectra was performed with the GRAMS program from Thermo Products.

The electrospray mass-spectra were recorded on an API-365 Perkin–Elmer Sciex at the “Service Commun de Spectrométrie de Masse” of the Paul Sabatier University, Toulouse.

Elemental analysis was realized with a Carlo Erba Strumenization analyser.

Table 1
UV–vis characteristics (λ_{max}, $\lambda_{shoulder}$ in nm, log ε) for compounds **IVa–t** in acetonitrile

IV	R	R^1	R^2	λ_{max} $\lambda_{shoulder}$	logε
a		CH_3	CH_3	570.5 538	5.1
b		CH_3	CH_2CH_3	571.0 531	4.9
c		CH_3		583.9 538	5.11
d		CH_3		581.3 536	4.72
e		CH_3		584.5 543	4.76
f		CH_3		592.1 551	–
g		CH_3		600.4 563	4.81
h		CH_3		592.7 548	4.75
i		CH_3		595.8 552	4.71
j		CH_2CH_3		585.8 542	4.76
k		CH_3		601.4 554	4.71
l		CH_3		593.3 551	4.72
m		CH_3		584.9 540	4.80
n		CH_3		577.6 –	–
o		CH_3		580.2 541	5.09
p		CH_3		597.1 554	4.80
q	CH_3	CH_3		595.2 550	–
r	CH_3		CH_3	566.2 530	4.67
s		CH_3	CH_3	570.0 –	4.75
t		CH_3		581.3 543	4.66

4.2. General experimental procedure

The starting products **II** and **III** were obtained by known methods [16,17].

4.3. Synthesis of acylated derivatives of ***Ia–b, f–k*** and cyanine dyes ***IVa–t***

The products are named by an easy running designation, but we present hereafter one example of systematic IUPAC nomenclature for **IVa**: 2-furan-2-yl-5-[1-(2-furan-2-yl-1-methyl-1*H*-[1,2,4]triazolo[5,1-*a*]isoindol-5-yl)-ethylidene]-1-methyl-5*H*-[1,2,4]triazolo[5,1-*a*]isoindol-1-ium perchlorate.

To the solution of salt **II** (0.7 mmol) in 3.5 ml of dioxane, 0.7 mmol of corresponding chloro-anhydride and 1.4 mmol of triethylamine were added. The mixture was heated to 100 °C for 1 h. The unreacted residue of the starting material was filtered off and washed twice with acetone. The combined filtrates were evaporated under reduced pressure and the obtained residue was separated by chromatography (silica gel L 100/250 mesh, eluent – dichloromethane–acetone (3:1)). Two types of products were isolated: acylated derivatives **Ia–b** and cyanine dyes **IVa–t**. Yields of acylated derivatives: **Ia** 76.6%, **Ib** 6%. Yields of cyanine dyes: from 7.6% (**IVf**) to 79.8% (**IVc**). Physical constants: melting point mp, ^{1}H NMR, chromatographic R_f and UV–vis (nm) data are given hereafter.

4.3.1. Acylated derivative ***Ia***

Mp 201 °C; ^{1}H NMR δ (DMSO-d_6) 4.172 (s, 3H, N–CH_3), 7.139 (t, 1H, H_{arom}), 7.317 (s, 1H, H_{arom}), 7.606 (m, 4H, H_{arom}), 7.784 (m, 5H, H_{arom}), 8.065 (d, 1H, H_{arom}); R_f 0.83 ($CHCl_3$/MeOH 9/1, 21 °C); UV–vis (CH_3CN) [λ, (log ε)] 391.75 (4.432). $C_{23}H_{15}Br_2N_3O$, M is 509.20. $M^+ = 509$; Analysis (calcd, found) % C (54.25, 54.30); H (2.97, 3.00); N (8.25, 8.27). Yield: 76.6%.

4.3.2. Acylated derivative ***Ib***

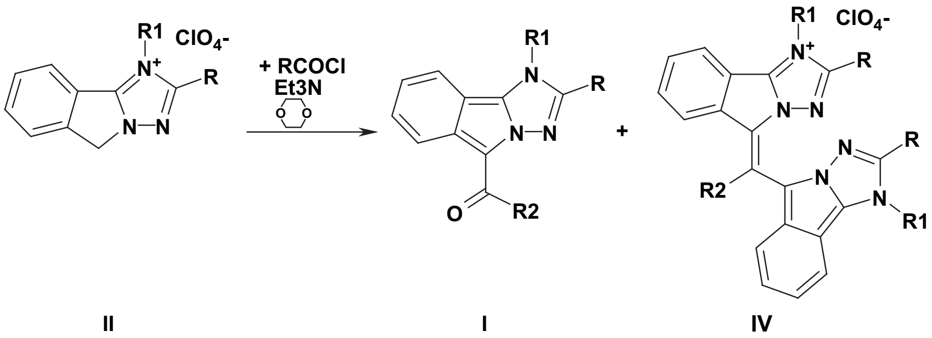
Mp 182 °C; ^{1}H NMR δ (DMSO-d_6) 1.188 (t, 3H, –CH_2CH_3), 3.232 (m, 2H, CH_2CH_3), 4.289 (s, 3H, N–CH_3), 6.779 (m, 1H, furan), 7.087 (m, 1H, H_{arom}), 7.321–7.433 (m, 3H, H_{arom}), 7.984 (m, 1H, furan), 8.333 (d, 1H, H_{arom}); R_f 0.85 ($CHCl_3$/MeOH 9/1, 21 °C); $C_{17}H_{17}N_3O_2$, M is 295.34. Analysis (calcd, found) % C (69.14, 69.17); H (4.38, 4.45); N (14.23, 14.25). Yield: 6%.

4.3.3. Cyanine dye ***IVa***

Mp 178 °C; ^{1}H NMR δ (DMSO-d_6) 3.436 (s, 3H, –CH_3), 4.425 (s, 6H, N–CH_3), 6.841 (m, 2H, furan), 6.956 (m, 2H, H_{arom}), 7.394 (m, 4H, H_{arom}), 7.457 (d, 2H, H_{arom}), 8.072 (s, 2H, furan), 8.333 (m, 2H, H_{arom}); ^{13}C NMR δ (DMSO-d_6) 17.58, 33.78, 110.22, 110.63, 112.64, 115.45, 120.80, 120.99, 122.93, 123.12, 129.37, 132.04, 132.58, 134.33, 138.93, 141.14, 146.47, 146.89; R_f 0.46 ($CHCl_3$/MeOH 9/1, 21 °C); $C_{30}H_{23}N_6O_8Cl$, M is 599.01. Analysis (calcd, found) % C (60.16, 60.19); H (3.87, 3.90); N (14.03, 14.09). Yield: 75.3%.

4.3.4. Cyanine dye ***IVb***

Mp 175 °C; ^{1}H NMR δ (DMSO-d_6) 1.410 (t, 3H, –CH_2CH_3), 3.750 (m, 1H, –CH_2CH_3), 4.216 (m, 1H, –CH_2CH_3), 4.396 (s, 6H, N–CH_3), 6.859 (m, 4H, H_{arom}), 7.376 (m, 6H, H_{arom}), 8.048 (s, 2H, furan), 8.301 (d, 2H, H_{arom}); R_f 0.43 ($CHCl_3$/MeOH 9/1, 21 °C); $C_{31}H_{25}ClN_6O_6$, M is 613.03. $M^+ = 513$. Analysis (calcd, found) % C (60.74, 60.80); H (4.11, 4.16); N (13.71, 13.78). Yield: 73%.



Scheme 2. Reaction of the 2-R^1-R^2-5*H*-[1,2,4]triazolo[5,1-*a*]isoindole perchlorate **II** with acyl chlorides (R, R^1, R^2 defined in Table 1).

4.3.5. Cyanine dye **IVc**

Mp 194 °C; ^{1}H NMR δ (DMSO-d_6) 4.427 (s, 6H, N–CH$_3$), 6.57 (d, 2H, H$_{arom}$), 6.65 (m, 2H, furan), 7.064 (s, 2H, furan), 7.241 (t, 2H, H$_{arom}$), 7.333 (t, 2H, H$_{arom}$), 7.435 (d, 2H, H$_{arom}$), 7.531 (d, 2H, H$_{arom}$), 7.905 (s, 2H, furan), 8.274 (d, 2H, H$_{arom}$); R_f 0.47 (CHCl$_3$/MeOH 9/1, 21 °C); $C_{36}H_{27}ClN_6O_6$, M is 675.11. Analysis (calcd, found) % C (64.05, 64.11); H (4.03, 4.08); N (12.45, 12.50). Yield: 79.8%.

4.3.6. Cyanine dye **IVd**

Mp 192 °C; ^{1}H NMR δ (DMSO-d_6) 3.972 (s, 3H, –O–CH$_3$), 4.425 (s, 6H, N–CH$_3$), 6.658 (m, 4H, H$_{arom}$), 7.063 (s, 2H, furan), 7.172 (d, 2H, H$_{arom}$), 7.265 (t, 2H, H$_{arom}$), 7.332 (t, 2H, H$_{arom}$), 7.563 (d, 2H, H$_{arom}$), 7.898 (s, 2H, furan), 8.278 (d, 2H, H$_{arom}$); R_f 0.45 (CHCl$_3$/MeOH 9/1, 21 °C); UV–vis (CH$_3$CN) 308 (4.06), 406 (3.58), 519* (4.31), 555 (4.80). $C_{36}H_{27}ClN_6O_7$, M is 691.11. Analysis (calcd, found) % C (62.57, 62.60); H (3.94, 3.98); N (12.16, 12.21). Yield: 73.2%.

4.3.7. Cyanine dye **IVe**

Mp 195.5 °C; ^{1}H NMR δ (DMSO-d_6) 4.435 (s, 6H, N–CH$_3$), 6.601 (d, 2H, H$_{arom}$), 6.676 (s, 2H, H$_{arom}$), 7.084 (s, 2H, H$_{arom}$), 7.283 (t, 2H, H$_{arom}$), 7.360 (t, 2H, H$_{arom}$), 7.429 (s, 2H, H$_{arom}$), 7.706 (s, 2H, H$_{arom}$), 7.919 (s, 2H, H$_{arom}$), 8.231 (d, 2H, H$_{arom}$); ^{13}C NMR δ (DMSO-d_6) 34.44, 110.00, 112.17, 113.04, 115.73, 117.45, 121.03, 121.61, 124.02, 129.50, 132.21, 135.19, 135.78, 139.46, 141.91, 146.44, 147.43; R_f 0.44 (CHCl$_3$/MeOH 9/1, 21 °C); $C_{35}H_{24}ClFN_6O_6$, M is 679.07. M$^+$ = 579; Analysis (calcd, found) % C (61.91, 61.97); H (3.56, 3.61); N (12.38, 12.44). Yield: 71.2%.

4.3.8. Cyanine dye **IVf**

Mp 196 °C; R_f 0.46 (CHCl$_3$/MeOH 9/1, 21 °C); $C_{36}H_{24}ClF_3N_6O_6$, M is 729.08. Analysis (calcd, found) % C (59.31, 59.36); H (3.32, 3.36); N (11.53, 11.58). Yield: 7.6%.

4.3.9. Cyanine dye **IVg**

Mp 191 °C; ^{1}H NMR δ (DMSO-d_6) 4.40 (s, 6H, N–CH$_3$), 6.67 (s, 2H, furan), 6. 89 (s, 1H, furan), 7.08 (m, 4H, H$_{arom}$), 7.39 (m, 5H, H$_{arom}$), 7.90 (s, 2H, furan), 8.09 (s, 1H, furan), 8.28 (m, 2H, H$_{arom}$); R_f 0.43 (CHCl$_3$/MeOH 9/1, 21 °C); $C_{33}H_{23}ClN_6O_7$, M is 651.04. M$^+$ = 551; Analysis (calcd, found) % C (60.88, 60.91); H (3.56, 3.59); N (12.91, 12.96). Yield: 76.5%.

4.3.10. Cyanine dye **IVh**

Mp 192.5 °C; ^{1}H NMR δ (DMSO-d_6) 4.425 (s, 6H, N–CH$_3$), 6.66 (s, 2H, furan), 6.77 (s, 2H, H$_{arom}$), 7.07 (s, 2H, H$_{arom}$), 7.35 (m, 5H, H$_{arom}$), 7.52 (s, 1H, thiophene), 7.90 (s, 2H, furan), 8.09 (s, 1H, thiophene), 8.31 (d, 2H, H$_{arom}$); R_f 0.43 (CHCl$_3$/MeOH 9/1, 21 °C); $C_{33}H_{23}ClN_6O_6S$,

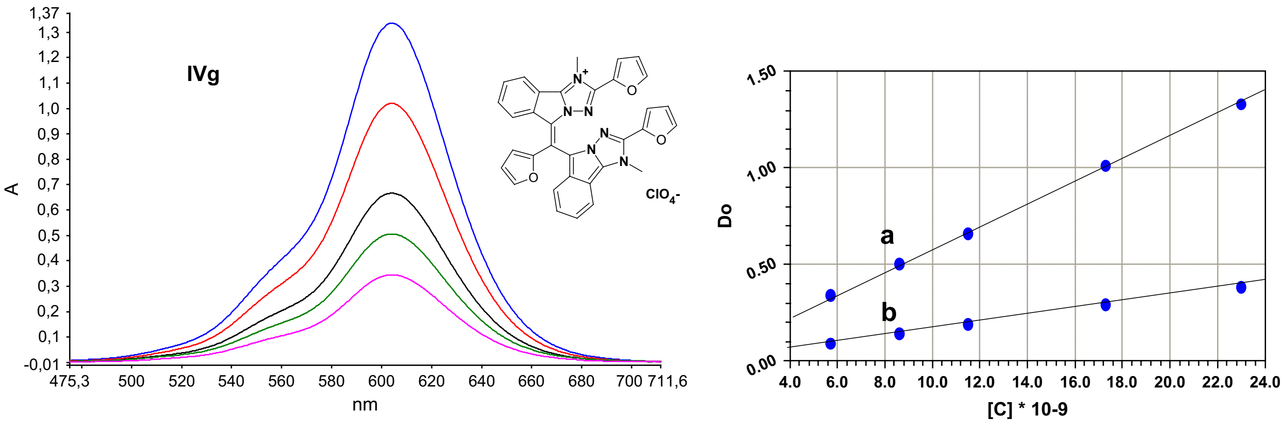


Fig. 1. Compound **IVg**: UV–vis spectra in dilution in CH$_2$Cl$_2$, concentration range: 2.3 × 10^{-8}–5.76 × 10^{-9} M. Linear correlation Do/[C] at (a) λ_{max} 587 nm, $R = 0.99988$ and (b) λ shoulder 540 nm $R = 0.99978$.

M is 667.10. Analysis (calcd, found) % C (59.42, 59.45); H (3.48, 3.53); N (12.60, 12.64). Yield: 77%.

4.3.11. Cyanine dye ***IVi***

Mp 194 °C; ^{1}H NMR δ (DMSO-d_6) 4.428 (s, 6H, N–CH_3), 6.617 (s, 2H, furan), 6.689 (s, 2H, H_{arom}), 7.079 (s, 2H, H_{arom}), 7.313 (t, 2H, H_{arom}), 7.394 (t, 2H, H_{arom}), 7.644 (s, 2H, H_{arom}), 7.938 (s, 2H, furan), 8.344 (d, 2H, H_{arom}), 8.830 (s, 2H, H_{arom}); R_f 0.42 ($CHCl_3$/MeOH 9/1, 21 °C); $C_{34}H_{24}ClN_7O_6$, M is 662.07. $M^+ = 562$. Analysis (calcd, found) % C (61.68, 61.71); H (3.65, 3.71); N (14.81, 14.83). Yield: 69.2%.

4.3.12. Cyanine dye ***IVj***

Mp 194 °C; ^{1}H NMR δ (DMSO-d_6) 1.678 (t, 6H, N–Et), 4.909 (q, 4H, N–Et), 6.65 (d, 2H, H_{arom}), 6.686 (m, 2H, furan), 6.983 (s, 2H, furan), 7.321 (t, 2H, H_{arom}), 7.396 (t, 2H, H_{arom}), 7.465 (m, 2H, H_{arom}), 7.784 (m, 2H, H_{arom}), 7.933 (s, 2H, furan), 8.28 (d, 2H, H_{arom}); R_f 0.43 ($CHCl_3$/MeOH 9/1, 21 °C); $C_{37}H_{28}FClN_6O_6$, M is 707.12. Analysis (calcd, found) % C (62.85, 62.87); H (3.99, 4.01); N (11.88, 11.92). Yield: 74.5%.

4.3.13. Cyanine dye ***IVk***

Mp 192.5 °C; ^{1}H NMR δ (DMSO-d_6) 4.409 (s, 6H, N–CH_3), 6.919 (s, 1H, furan), 7.097 (s, 1H, furan), 7.242 (m, 2H, H_{arom}), 7.422 (m, 5H, H_{arom}), 7.773 (m, 5H, H_{arom}), 8.231 (s, 1H, furan), 8.332 (d, 2H, H_{arom}); ^{13}C NMR δ (DMSO-d_6) 34.27, 108.45, 111.88, 114.30, 119.54, 120.96, 121.55, 124.25, 125.13, 129.39, 129.73, 131.68, 132.25, 134.86, 142.16, 147.79, 150.06; R_f 0.46 ($CHCl_3$/MeOH 9/1, 21 °C); $C_{33}H_{23}ClN_6S_2O_5$, M is 683.17. $M^+ = 583$; Analysis (calcd, found) % C (58.02, 58.05); H (3.39, 3.41); N (12.30, 12.31). Yield: 73.2%.

4.3.14. Cyanine dye ***IVl***

Mp 195 °C; ^{1}H NMR δ (DMSO-d_6) 4.413 (s, 6H, N–CH_3), 6.803 (m, 2H, thiophene), 7.231 (m, 2H, H_{arom}), 7.333–7.384 (m, 4H, H_{arom}), 7.441 (s, 1H, thiophene), 7.556 (s, 1H, thiophene), 7.768 (m, 4H, H_{arom}), 8.118 (s, 1H, thiophene), 8.332 (d, 2H, H_{arom}); R_f 0.42 ($CHCl_3$/MeOH 9/1, 21 °C); $C_{33}H_{23}ClN_6S_3O_4$, M is 699.23. $M^+ = 599$; Analysis (calcd, found) % C (59.29, 59.31); H (3.32, 3.34); N (12.02, 12.06). Yield: 72%.

4.3.15. Cyanine dye ***IVm***

Mp 194 °C; ^{1}H NMR δ (DMSO-d_6) 4.426 (s, 6H, N–CH_3), 6.612 (d, 2H, H_{arom}), 7.219–7.360 (m, 6H, H_{arom}), 7.455 (d, 2H, H_{arom}), 7.565 (d, 2H, H_{arom}), 7.770 (m, 4H, thiophene), 8.310 (d, 2H, H_{arom}); R_f 0.43 ($CHCl_3$/MeOH 9/1, 21 °C); $C_{36}H_{27}ClN_6S_2O_4$, M is 707.24. $M^+ = 607$; Analysis (calcd, found) % C (61.14, 61.17); H (3.85, 3.87); N (11.88, 11.91). Yield: 73.8%.

4.3.16. Cyanine dye ***IVn***

Mp 205 °C; R_f 0.35 ($CHCl_3$/MeOH 9/1, 21 °C); UV–vis (CH_3CN) 309 (3.69), 369 (3.40), 562 (4.26). $C_{40}H_{35}Cl_3N_8O_{12}$, M is 925.13. Analysis (calcd, found) % C (51.88, 51.93); H (3.81, 3.85); N (12.10, 12.12). Yield: 65.2%.

4.3.17. Cyanine dye ***IVo***

Mp 199 °C; ^{1}H NMR δ (DMSO-d_6) 4.275 (s, 6H, N–CH_3), 6.576 (m, 2H, H_{arom}), 7.249 (t, 2H, H_{arom}), 7.329 (t, 2H, H_{arom}), 7.465 (d, 2H, H_{arom}), 7.543 (d, 2H, H_{arom}), 7.606 (s, 8H, H_{arom}), 8.257 (d, 2H, H_{arom}); R_f 0.44 ($CHCl_3$/MeOH 9/1, 21 °C); $C_{40}H_{29}Cl_3N_6O_4$, M is 774.07. $M^+ = 665$; Analysis (calcd, found) % C (62.88, 62.93); H (3.83, 3.85); N (11.00, 11.02). Yield: 64.5%.

4.3.18. Cyanine dye ***IVp***

Mp 203 °C; ^{1}H NMR δ (DMSO-d_6) 4.266 (s, 6H, N–CH_3), 6.926 (s, 1H, furan), 7.074 (s, 1H, furan), 7.414 (m, 4H, H_{arom}), 7.542 (m, 4H, H_{arom}), 7.743 (m, 6H, H_{arom}), 8.111 (s, 1H, furan), 8.295 (d, 2H, H_{arom}); R_f 0.43 ($CHCl_3$/MeOH 9/1, 21 °C); $C_{37}H_{25}Br_2ClN_6O_5$, M is 821.91. Analysis (calcd, found) % C (53.61, 53.53); H (3.04, 3.07); N (10.14, 10.18). Yield: 24.3%.

4.3.19. Cyanine dye ***IVq***

Mp 168 °C; R_f 0.46 ($CHCl_3$/MeOH 9/1, 21 °C); $C_{27}H_{23}IN_6O$, M is 574.43. Analysis (calcd, found) % C (56.46, 56.47); H (4.04, 4.07); N (14.63, 14.67). Yield: 55.6%.

4.3.20. Cyanine dye ***IVr***

Mp 165 °C; R_f 0.44 ($CHCl_3$/MeOH 9/1, 21 °C); $C_{36}H_{31}BrN_6$, M is 627.29. Analysis (calcd, found) % C (68.90, 68.92); H (4.98, 5.02); N (13.39, 13.40). Yield: 58.1%.

4.3.21. Cyanine dye ***IVs***

Mp 193 °C; ^{1}H NMR δ (DMSO-d_6) 3.431 (s, 3H, CH_3), 4.271 (s, 6H, N–CH_3), 7.424 (m, 4H, H_{arom}), 7.682 (m, 6H, H_{arom}), 7.863 (m, 6H, H_{arom}), 8.331 (d, 2H, H_{arom}); R_f 0.42 ($CHCl_3$/MeOH 9/1, 21 °C); $C_{34}H_{27}ClN_6O_4$, M is 619.09. Analysis (calcd, found) % C (65.96, 65.99); H (4.40, 4.42); N (13.57, 13.61). Yield: 71.5%.

4.3.22. Cyanine dye ***IVt***

Mp 199 °C; R_f 0.45 ($CHCl_3$/MeOH 9/1, 21 °C); $C_{39}H_{36}ClF_3N_6O_4$, M is 735.13. $M^+ = 735.2$ Analysis (calcd, found) % C (63.72, 65.97); H (3.56, 3.60); N (11.43, 11.48). Yield: 78.5%.

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