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New Luminescent Dyes from the Series of 1,3,7-Substituted Dibenzothiophene-5,5-diones

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Abstract—Preparation method was developed and a series of new linear polyconjugated compounds was obtained with (1,3-benzoxazol-2-yl)ethenyl, (5-oxo-2-phenyl-1,3-oxazolidine)methyl moieties in the positions *3, 7* of dibenzothiophene-5,5-dione frame and with peripheral alkoxy- and alkylamine substituents in the position *1*. Compounds obtained possess a strong luminescence in solutions, in the solid state, and exhibit electroluminescent properties.

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Linear polyconjugated organic compounds have attracted high attention of researchers in the last decades since they are connected with the new vigorously developing technological field, molecular electronics. Due to their structural versatility and a wide range of specific optical, electrochemical, and electric properties they are extensily utilized in designing new means of information storage (OLED) [1, 2], in production of organic field transistors [3, 4], devices for transformation of the solar energy [5], for storage and processing of information [6] etc.

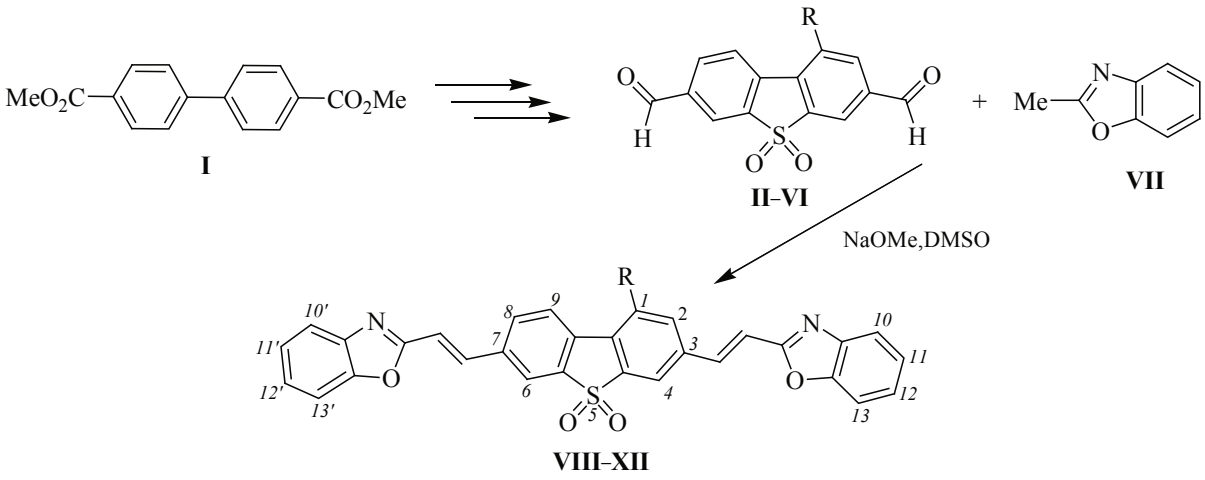
In extension of research on the investigation of electroactive poly-π-conjugated compounds [7–10] we report here on the results of the study of properties and the synthesis of a series of new linear polyconjugated compounds based on dibenzothiophene.

We investigated linear molecules with the 5,5-dioxodibenzothiophene core connected with chains of conjugated electron-donor and electron-acceptor groups, in particular, compounds containing in the conjugation chain a 1,3-oxazole moiety. Due to the electron-deficient nature of the oxazole moiety and of SO_2 group of the dibenzothiophene-5,5-dione fragment these compounds should possess good electronic conductivity, and that is very important in designing light-emitting diodes. Besides the planar conformation of the dibenzothiophene ring system governs the high π-conjugation along the total molecular chain, and this permits the prediction in such molecules of electroluminescent properties. We presumed that the introduction of additional electron-donor groups into the position *1* of the dibenzothiophene framework would significantly affect the optical characteristics of compounds synthesized and would make it possible to obtain a series of efficient luminophores radiating in a wide spectral range.

The procedure of the synthesis of initial 1-alkoxy- or 1-amino-5,5-dioxodibenzothiophene-3,7-dicarbaldehydes **II–VI** from dimethyl biphenyl-4,4'-dicarboxylate we have described before [7].

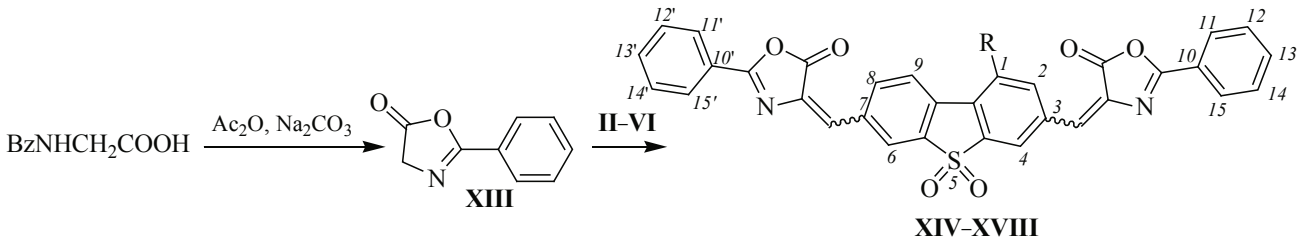
The introduction of 1,3-benzoxazol-2-ylethenyl fragments into the molecule of dibenzothiophene-5,5-dione was performed in one stage by the condensation of dicarbaldehydes **II–VI** with a slight excess of 2-methylbenzoxazole (**VII**) in DMSO in the presence of an equimolar quantity of sodium methylate as a base (Scheme 1). As a result the most stable *trans-trans*-isomers of 1-substituted 3,7-bis[2-(1,3-benzoxazol-2-yl) ethenyl]dibenzothiophene-5,5-diones **VIII–XII** formed in good yield(75–82%) and with high stereoselectivity. The formation of the thermodynamically more stable isomers was confirmed by the ^{1}H NMR data. The signals of the ethenyl protons are split with large coupling constants characteristic of the *trans* configuration.

Scheme 1.



R = OMe (**II, VIII**), OC_6H_{13} (**III, IX**), $N(Me)_2$ (**IV, X**), NHC_4H_9 (**V, XI**), NHC_6H_{13} (**VI, XII**).

Scheme 2.



R = OMe (**II, XIV**), OC_6H_{13} (**III, XV**), $N(Me)_2$ (**IV, XVI**), NHC_4H_9 (**V, XVII**), NHC_6H_{13} (**VI, XVIII**).

The synthesis of derivatives containing methylidene-1,3-oxazol-5-one fragments is presented in Scheme 2.

The attempt to obtain azalactones **XIV–XVIII** under the conditions of the classic Erlenmeyer–Plächl reaction from hippuric acid and dialdehydes **II–VI** in the presence of sodium acetate in acetic anhydride provided the target compounds in low yield, less than 30%. We succeeded in notable increase in the yield when the condensation reaction was carried out in two steps. The reaction was started by heating hippuric acid and sodium carbonate in acetic anhydride till complete dissolution. Then to the solution of 2-phenyl-1,3-oxazol-5-one (**XIII**) formed in the first stage were added dialdehydes **II–VI** whose successive condensation to the activated methylene group in oxazolone **XIII** furnished substituted dibenzothiophenes **XIV–XVIII** in 60–82% yields.

The stereoselectivity of the reaction was studied applying HPLC method. The analysis of the homogeneity of products was performed on 1-hexyloxy **XV** and 1-butylamino **XVII** derivatives. The detection was carried out both by the absorption in the UV region and by the ion current using mass detector. In the chromatogram with the detection by ion current for both compounds was found a single peak at the detection of positive as well as negative ions.

The fragmentation of the corresponding ions (MS^2 experiment) revealed some peculiarities in the fragmentation of the protonated molecules and additionally confirmed the presence of a single isomer corresponding to the main peak. The characteristic feature of the fragmentation of protonated molecules of compounds **XV, XVII** consists in a successive ejection of carbon monoxide elements from the oxazolone ring and in the elimination of the phenyl group.

The structure of compounds obtained was also confirmed by the IR and ^1H NMR spectra. The IR spectra of both groups of compounds **VIII–XII** and **XIV–XVIII** contain strong absorption bands at 1575–1500 and 1560–1500 cm^{-1} characteristic of the bending vibrations

of the ring fragment –N=C–O–, very strong bands [1340–1310, 1165–1150 (**IV**), 1355–1315, 1185–1155 cm^{-1}] of symmetric and antisymmetric vibrations of the O=S=O group, and the bands of the stretching vibrations of CH in the aromatic rings in the region 3110–3035 cm^{-1}. In the ^1H NMR spectra of 1-alkoxy and 1-alkylamino derivatives **VIII–XII, XIV–XVIII** in the region 0.91–4.45 ppm signals were observed belonging to the protons of methyl and methylene groups of the alkyl moieties with the characteristic multiplicity. The signals of NH protons in the spectra of compounds appear as broadened singlets in the region 5.85–6.40 ppm. The aromatic protons of the dibenzothiophene-5,5-dione fragment appear in the most downfield part of the spectrum (7.70–8.85 ppm), the protons at $C^{6,8,9}$ are clearly identified by the multiplicity of the signals. The protons $H^{2,4}$ in the spectra of 1-alkylamino derivatives **X–XII, XVI–XVIII** give rise to doublets with small coupling constants (1–1.5 Hz) and apparently the most upfield signal belongs to the proton H^2 owing to the shielding effect of the amino group in the *ortho*-position. The multiplets of the rest of the aromatic protons of the 2-phenyl-1,3-oxazolin-5-one and 1,3-benzoxazol-2-yl fragments are located in the region 7.30–8.16 ppm.

All compounds synthesized **VIII–XII, XIV–XVIII** possess a strong luminescence in solutions and in the solid state. Depending on the nature of substituents in the positions *1*, *3, 7* of the dibenzothiophene framework and on their combination the maximum of the photoluminescence of the solution lies between 465 and 632 nm including all visible spectrum range (see the table). As seen from the reported data the introduction of the electron-donor alkylamine group in the position *1* of the dibenzothiophene fragment results in the shift of the luminescence maximum to the longwave region and in the sharp growth of the value of the Stokes shift which in the case of compound **XVIII** reached abnormally large magnitude of 208 nm. Besides amino derivatives **X–XII, XVI–XVIII** show a strong solvatochromic effect, and on replacement of toluene by highly polar dimethylformamide a red shift is observed of the luminescence maximum (more than by 50 nm) and a strong blue shift in the absorption spectra.

The possibility to use alkoxy derivatives **IX, XIV** as emitting layers in the organic light-emitting devices was shown by an example of the electroluminescence material of the structure ITO/NPB (60 nm)/**IX** (**XIV**)(20 nm)/TPBi (10 nm)/Alq3 (30 nm)/LiF (1nm)/Al. The maximum electroluminescence of these compounds is observed in the more longwave region, at 544 and 540 nm respectively. The electroluminescence properties of amino derivatives are under study.

EXPERIMENTAL

Melting points were measured on a Koeffler heating block equipped with an electronic thermometer Hanna HI 93530. ^1H NMR spectra were registered from DMSO-d_6 solutions on spectrometers Bruker Avance-500 (500 MHz) and Tesla BS-587A (100 MHz) using TMS as

UV absorption and photoluminescence of compounds **VIII–XII, XIV–XVII**

Compound no.	Absorption, λ_{max}, nm		Luminescence, λ_{max}, nm	
	toluene	DMF	toluene	DMF
VIII	380, 430	390, 412	466	465
IX	379, 430	390, 411	467	466
X	407, 437	362, 401	499	549
XI	399, 445	352, 434	497	546
XII	397, 456	344, 439	498	547
XIV	469, 499	352, 415	521	524
XV	468, 499	344, 406	523	519
XVI	458, 486	355, 402	580	614
XVII	439, 506	358, 418	573	627
XVIII	440, 505	364, 424	575	632

internal reference. IR spectra were recorded on a spectrophotometer Specord M-80 from pellets with KBr. UV spectra and fluorescence sperctra were obtained on a spectrofluorimeter Solar CM2203 (cell thickness 1 cm). Mass spectra (MS and MS^2) were taken on an instrument HPLC Accela with a mass detector LCQ-Fleet (three-dimension ion trap) in the chemical ionization mode at the atmospheric pressure (APCI), detection of positive and negative ions, CID 35%. HPLC conditions: column Hypersil Gold (50 mm × 2.1 mm × 1.9 μm), mobil phase 95% MeCN (100 μl/min), the amount of the injected probe 30 ng. The purification and drying of solvents and reagents was carried out by common methods [11]. The reaction progress was monitored by TLC on plastic plates with silica gel 60 A, F_{254} (Merck Art. 7734), eluent toluene, development under UV irradiation at 254 and 365 nm.

Compounds VIII–XII. General procedure. To a solution of 1 mmol of dialdehyde **II–VI** and 270 mg (2 mmol) of 2-methyl-1,3-benzoxazol in 15 ml of anhydrous DMSO was added at stirring a solution of 90 mg (2 mmol) of MeONa in 5 ml of methanol. The reaction mixture was stirred for 16 h at 40–50°C. The precipitate was filtered off, washed with water, 5% HCl, and again with water, then it was recrystallized from DMSO.

3,7-Bis[(*E*)-2-(1,3-benzoxazol-2-yl)ethenyl]-1-methoxy-5*H*-dibenzo[*b*,*d*]thiophene-5,5-dione (VIII). Yield 91% (yellow crystals), mp >380°C. IR spectrum, cm^{-1}: 2945, 2870, 1650, 1600, 1595, 1540, 1465, 1420, 1365, 1320, 1260, 1175, 1065, 1025, 985, 955, 910, 875, 855, 780, 765, 735. ^1H NMR spectrum, δ, ppm: 4.17 s (3H, CH_3O), 7.39 t (2H, $H^{11,11'}/H^{12,12'}$, *J* 5.8 Hz), 7.42 t (2H, $H^{11,11'}/H^{12,12'}$, *J* 7.0 Hz), 7.58 d (1H, =CH–, *J* 16.5 Hz), 7.69 d (1H, =CH–, *J* 16.5 Hz), 7.74 d (2H, $H^{10,10'}/H^{13,13'}$, *J* 8.0 Hz), 7.77 d (2H, $H^{10,10'}/H^{13,13'}$, *J* 8.0 Hz), 7.89 s (1H, $H^2/H^4/H^6$), 7.92 d (1H, =CH–, *J* 15.5 Hz), 7.94 d (1H, =CH–, *J* 15.5 Hz) 8.09 s (1H, $H^2/H^4/H^6$), 8,15 d (1H, H^8/H^9, *J* 8.0 Hz), 8.32 d (1H, H^8/H^9, *J* 8.0 Hz), 8.51 s (1H, $H^2/H^4/H^6$). Mass spectrum, *m/z*: 533 $[M + 1]^+$. *M* 532. $C_{31}H_{20}N_2O_5S$. *M* 532.57.

3,7-Bis[(*E*)-2-(1,3-benzoxazol-2-yl)ethenyl]-1-hexyloxy-5*H*-dibenzo[*b*,*d*]thiophene-5,5-dione (IX). Yield 88%, mp 269–271°C. IR spectrum, cm^{-1}: 2940, 2870, 1640, 1595, 1575, 1535, 1455, 1415, 1355, 1310, 1245, 1190, 1165, 1045, 1015, 975, 945, 900, 865, 840, 775, 750, 730. ^1H NMR spectrum, δ, ppm: 0.91 t (3H, CH_3, *J* 7.0 Hz), 1.31–1.45 m (4H, CH_2), 1.54 m (2H, CH_2), 1.93 m (2H, OCH_2), 4.34 t (2H, OCH_2, *J* 6.5 Hz), 7.37 t (2H, $H^{11,11'}/H^{12,12'}$, *J* 5.8 Hz), 7.42 t (2H, $H^{11,11'}/H^{12,12'}$, *J* 7.0 Hz), 7.55 d (1H, =CH–, *J* 16.5 Hz), 7.65 d (1H, =CH–, *J* 16.5 Hz), 7.72 d (2H, H10, $H^{10,10'}/H^{13,13'}$, *J* 8.0 Hz), 7.76 d (2H, $H^{10,10'}/H^{13,13'}$, *J* 8.0 Hz), 7.83 c (1H, $H^2/H^4/H^6$), 7.85 d (1H, =CH–, *J* 15.5 Hz), 7.86 d (1H, =CH–, *J* 15.5 Hz), 8.07 s (1H, $H^2/H^4/H^6$), 8.11 d (1H, H^8/H^9, *J* 8.0 Hz), 8.23 d (1H, H^8/H^9, *J* 8.0 Hz), 8.51 s (1H, $H^2/H^4/H^6$). Mass spectrum, *m/z*: 603 $[M + 1]^+$. *M* 602. $C_{36}H_{30}N_2O_5S$. *M* 602.70.

3,7-Bis[(*E*)-2-(1,3-benzoxazol-2-yl)ethenyl]-1-(dimethylamino)-5*H*-dibenzo[*b*,*d*]thiophene-5,5-dione (X). Yield 81%, mp 335–336°C. IR spectrum, cm^{-1}: 3075, 3005, 2965, 2800, 1645, 1595, 1575, 1535, 1480, 1455, 1410, 1355, 1305, 1250, 1190, 1170, 1120, 1055, 1020, 980, 950, 900, 870, 840, 775, 755, 735. ^1H NMR spectrum, δ, ppm: 2.87 s (6H, Me_2N), 7.40 t (2H, $H^{11,11'}/H^{12,12'}$, *J* 7.8 Hz), 7.43 t (2H, $H^{11,11'}/H^{12,12'}$, *J* 7.5 Hz), 7.60 d (1H, =CH–, *J* 16.0 Hz), 7.65 d (1H, =CH–, *J* 16.0 Hz), 7.74 d (2H, $H^{10,10'}/H^{13,13'}$, *J* 7.5 Hz), 7.78 d (2H, $H^{10,10'}/H^{13,13'}$, *J* 7.5 Hz), 7.90 s (1H, $H^2/H^4/H^6$), 7.92 d (2H, CH=CH, *J* 16.0 Hz), 8.17 s (1H, $H^2/H^4/H^6$), 8.18 d (1H, H^8/H^9, *J* 8.0 Hz), 8.33 d (1H, H^8/H^9, *J* 8.0 Hz), 8.54 s (1H, $H^2/H^4/H^6$). Mass spectrum, *m/z*: 546 $[M + 1]^+$. *M* 545. $C_{32}H_{23}N_3O_4S$. *M* 545.61.

3,7-Bis[(*E*)-2-(1,3-benzoxazol-2-yl)ethenyl]-1-(butylamino)-5*H*-dibenzo[*b*,*d*]thiophene-5,5-dione (XI). Yield 82%, mp 327–329°C. IR spectrum, cm^{-1}: 3415, 3075, 3035, 2975, 2940, 2880, 2865, 1635, 1590, 1570, 1545, 1490, 1470, 1450, 1440, 1420, 1350, 1290, 1235, 1215, 1185, 1157, 1150, 1115, 1080, 1065, 1005, 970, 945, 895, 880, 855, 835, 815, 760, 740, 715. ^1H NMR spectrum, δ, ppm: 1.02 t (3H, CH_3, *J* 6.8 Hz), 1.54 m (2H, CH_2), 1.78 m (2H, $NCH_2C\underline{H}_2$), 3.44 m (2H, NCH_2), 5.85 s (1H, NH), 7.37–7.47 m (4H, $H^{11,11',12,12'}$), 7.43 d (1H, =CH–, *J* 17.0 Hz), 7.50 d (1H, =CH–, *J* 17.0 Hz), 7.70 d (2H, $H^{10,10'}/H^{13,13'}$, *J* 6.5 Hz), 7.75 d (2H, $H^{10,10'}/H^{13,13'}$, *J* 6.5 Hz), 7.64 s (1H, $H^2/H^4/H^6$), 7.82 s (1H, $H^2/H^4/H^6$), 7.90 d (1H, =CH–, *J* 17.0 Hz), 7.94 d (1H, =CH–, *J* 17.0 Hz), 8.11 d (1H, H^8/H^9, *J* 8.0 Hz), 8.27 d (1H, H^8/H^9, *J* 8.0 Hz), 8.37 c (1H, $H^2/H^4/H^6$). Mass spectrum, *m/z*: 574 $[M + 1]^+$. $C_{34}H_{27}N_3O_4S$. *M* 537.67.

3,7-Bis[(*E*)-2-(1,3-benzoxazol-2-yl)ethenyl]-1-(hexylamino)-5*H*-dibenzo[*b*,*d*]thiophene-5,5-dione (XII). Yield 81%, mp 278–280°C. IR spectrum, cm^{-1}: 3080, 2970, 2940, 2870, 1645, 1600, 1575,1530, 1475, 1455, 1420, 1355, 1305, 1245, 1185, 1160, 1120,1065, 1015, 975, 945, 900, 865, 830, 775, 755, 725. ^1H NMR spectrum, δ, ppm: 0.90 t (3H, CH_3, *J* 6.8 Hz), 1.29–

1.40 m (4H, CH_2), 1.46 m (2H, CH_2), 1.71 m (2H, CH_2), 3.15–3.55 m (2H, NCH_2), 6.20 t (1H, NH, *J* 5.3 Hz), 7.40–7.44 m (4H), 7.46 s (1H, H^2/H^4), 7.62 d (1H, =CH–, *J* 16.5 Hz), 7.64 d (1H, =CH–, *J* 16.5 Hz), 7.73–7.77 m (4H), 7.82 s (1H, H^2/H^4), 7.93 d (1H, =CH–, *J* 16.0 Hz), 7.95 d (1H, =CH–, *J* 16.0 Hz), 8.18 d (1H, H^8, J_1 8.5, J_2 1.0 Hz), 8.27 d (1H, H^9, *J* 8.5 Hz), 8.55 d (1H, H^6, *J* 1.0 Hz). Mass spectrum, *m/z*: 602 $[M+1]^+$. $C_{36}H_{31}N_3O_4S$. *M* 601.71.

Compounds XIV–XVIII. *General procedure.* A mixture of 2.0 mmol of benzoylaminoacetic acid and 2.0 mmol of sodium carbonate in 15 ml of acetic anhydride was boiled for 20 min. Then still at heating to the solution was added an appropriate aldehyde **II–VII**. Several minutes later the reaction mixture get orange or red depending on aldehyde used. The reaction mixture was stirred at 100–110°C over 5 h, then it was cooled and poured on ice. The precipitated crystals were filtered off, washed with water and hot ethanol, and recrystallized from DMSO.

4,4'-[(1-Methoxy-5,5-dioxo-5*H*-dibenzo[*b,d*]-thiophene-3,7-diyl)di(methylidene)]bis[2-phenyl-oxazole-5(4*H*)-one] (XIV). Yield 80%, mp 345°C (decomp). IR spectrum, cm^{-1}: 3120, 3075, 2910, 1815, 1665, 1610, 1575, 1500, 1455, 1420, 1385, 1340, 1300, 1190, 1175, 1125, 1110, 1080, 1060, 1020, 1005, 930, 895, 880, 860, 790, 775, 720. ^1H NMR spectrum, δ, ppm: 4.23 s (3H, CH_3O), 7.50 s (1H, CH=C), 7.51 s (1H, CH=C), 7.68 m (4H), 7.772 t (1H, $H^{13}/H^{13'}$ *J* 7.0 Hz), 7.776 t (1H, $H^{13}/H^{13'}$, *J* 7.0 Hz), 8.17 m (4H), 8.43 s (1H, H^2/H^4), 8.46 s (1H, H^2/H^4), 8.52 d (1H, H^9, *J* 8.5 Hz), 8.69 d.d (1H, H^8, J_1 8.5, J_2 1.5 Hz), 8.83 d (1H, H^6, *J* 1.5 Hz). Mass spectrum, *m/z*: 589 $[M+1]^+$. *M* 588. $C_{33}H_{20}N_2O_7S$. *M* 588.59.

4,4'-[(1-Hexyloxy-5,5-dioxo-5*H*-dibenzo[*b,d*]-thiophene-3,7-diyl)di(methylidene)]bis[2-phenyl-oxazole-5(4*H*)-one] (XV). Yield 82%, mp 280°C (decomp.). IR spectrum, cm^{-1}: 3120, 3075, 2910, 2940, 2875, 1800, 1660, 1605, 1560, 1490, 1455, 1420, 1380, 1330, 1300, 1235, 1190, 1170, 1155, 1125, 1080, 1050, 1000 895, 870, 790, 775, 710. ^1H NMR spectrum, δ, ppm: 0.93 t (3H, CH_3, *J* 7.0 Hz), 1.36–1.44 m (4H, CH_2), 1.55–1.64 m (2H, CH_2), 1.98–2.04 m (2H, CH_2), 4.45 t (2H, OCH_2, *J* 6.5 Hz), 7.48 s (1H, CH=C), 7.50 s (1H, CH=C), 7.68 m (4H), 7.77 t (1H, $H^{13}/H^{13'}$, *J* 7.0 Hz), 7.78 t (1H, H $H^{13}/H^{13'}$, *J* 7.5 Hz), 8.16 m (4H), 8.42 s (1H, H^2/H^4), 8.44 s (1H, H^2/H^4), 8.47 d (1H, H^9, *J* 8.5 Hz), 8.65 d.d (1H, H^8, J_1 8.5, J_2 1.5 Hz), 8.83 d (1H, H^6, *J* 1.5 Hz). Mass spectrum, *m/z* (I_{rel}, %): 659 $[M+1]^+$ (100), 698 $[M-1+MeCN]^-$ (14), 658 $[M]^-$ (100), 573 $[M-1-3CO]^+$ (26), 525 $[M-2CO-Ph]^-$ (21). Mass spectrum MS^2659; *m/z* (I_{rel}, %): 631 $[M+1-CO]^+$ (100), 575 $[M+1-3CO]^+$ (16), 526 $[M+1-2CO-Ph]^+$ (16). *M* 658. $C_{38}H_{30}N_2O_7S$. *M* 658.72.

4,4'-[(1-Dimethylamino-5,5-dioxo-5*H*-dibenzo-[*b,d*]thiophene-3,7-diyl)di(methylidene)]bis[2-phenyl-oxazole-5(4*H*)-one] (XVI). Yield 65%, mp 320°C (decomp.). IR spectrum, cm^{-1}: 3450, 3115, 3070, 2905, 2945, 2875, 1810, 1665, 1605, 1550, 1480, 1445, 1410, 1380, 1335, 1300, 1235, 1195, 1155, 1120, 1085, 1050, 1000, 885, 870, 790, 770, 715. ^1H NMR spectrum, δ, ppm: 2.93 s (6H, Me_2N), 7.52 s (1H, CH=C), 7.53 s (1H, CH=C), 7.70 m (4H), 7.78 t (1H, $H^{13}/H^{13'}$, *J* 7.5 Hz), 7.78 t (1H, $H^{13}/H^{13'}$, *J* 7.5 Hz), 8.17 m (4H), 8.48 d (1H, H^9, *J* 8.5 Hz), 8.51 s (1H, H^2/H^4), 8.57 s (1H, H^2/H^4), 8.83 d.d (1H, H^8, J_1 8.5, J_2 1.5 Hz), 8.84 s (1H, H^6, *J* 1.5 Hz). Mass spectrum, *m/z*: 602 $[M+1]^+$. $C_{34}H_{23}N_3O_6S$. *M* 601.63.

4,4'-[(1-Butylamino-5,5-dioxo-5*H*-dibenzo-[*b,d*]thiophene-3,7-diyl)di(methylidene)]bis[2-phenyl-oxazole-5(4*H*)-one] (XVII). Yield 68%, mp 300°C (decomp.). IR spectrum, cm^{-1}: 3450, 3070, 2975, 2945, 2880, 1805, 1660, 1605, 1560, 1495, 1455, 1420, 1380, 1335, 1305, 1240, 1180, 1160, 1125, 1085, 1040, 1090, 990, 890, 790, 775, 710. ^1H NMR spectrum, δ, ppm: 1.0 t (3H, CH_3, *J* 7.0 Hz), 1.51 m (2H, CH_2), 1.78 m (2H, CH_2), 3.42 m (2H, NCH_2), 6.40 c (1H, NH), 7.16 s (1H, CH=C), 7.24 s (1H, CH=C), 7.52 m (4H), 7.76 t (1H, $H^{13}/H^{13'}$, *J* 7.5 Hz), 7.77 t (1H, $H^{13}/H^{13'}$, *J* 7.5 Hz), 8.15 m (4H), 8.17 d (1H, H^9, *J* 8.5 Hz), 8.30 s (1H, H^2/H^4), 8.41 s (1H, H^2/H^4), 8.71 d.d (1H, H^8, J_1 8.5, J_2 1.5 Hz), 8.82 s (1H, H^6, *J* 1.5 Hz). Mass spectrum *m/z* (I_{rel}, %): 630 $[M+1]^+$ (100), 628 $[M-1]^-$ (100), 496 $[M-2CO-Ph]^-$ (20). Mass spectrum MS^2630; *m/z* (I_{rel}, %): 612 $[M+1-H_2O]^+$ (12), 602 $[M+1-CO]^+$ (100), 574 $[M+1-2CO]^+$ (67), 497 $[M+1-2CO-Ph]^+$ (16). *M* 629. $C_{36}H_{27}N_3O_6S$. *M* 629.69.

4,4'-[(1-Hexylamino-5,5-dioxo-5*H*-dibenzo-[*b,d*]thiophene-3,7-diyl)di(methylidene)]bis[2-phenyl-oxazole-5(4*H*)-one] (XVIII). Yield 66%, mp 290°C (decomp.). IR spectrum, cm^{-1}: 3445, 3050, 2965, 2940, 2880, 1805, 1665, 1605, 1565, 1495, 1455, 1415, 1370, 1330, 1305, 1240, 1175, 1160, 1120, 1085, 1040, 1080, 995, 890, 785, 775, 715. ^1H NMR spectrum, δ, ppm: 0.88 t (3H, CH_3, *J* 7.0 Hz), 1.34 m (4H, CH_2), 1.48 m (2H, CH_2), 1.79 m (2H, CH_2), 3.35 m (2H, NCH_2), 6.34 s (1H, NH), 7.47 s (1H, CH=C), 7.50 s (1H, CH=C), 7.67 m

(4H), 7.75 t (1H, $H^{13}/H^{13'}$, *J* 7.5 Hz), 7.77 t (1H, $H^{13}/H^{13'}$, *J* 7.5 Hz), 8.13 m (4H), 8.16 d (1H, H^{9}, *J* 8.5 Hz), 8.39 s (1H, H^{2}/H^{4}), 8.67 s (1H, H^{2}/H^{4}), 8.83 d.d (1H, H^{8}, J_1 8.5, J_2 1.5 Hz), 8.84 s (1H, H^{6}, *J* 1.5 Hz). Mass spectrum, *m/z*: 658 $[M + 1]^+$. $C_{38}H_{31}N_3O_6S$. *M* 657.74.

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