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Synthesis and characterisation of long wavelength-absorbing donor/acceptor-substituted methine dyes

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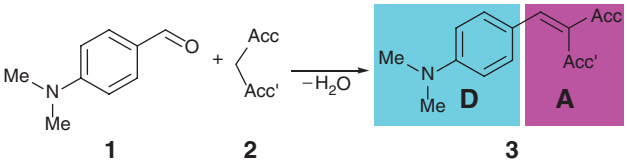
Abstract: By the reaction of aromatic or heteroaromatic formyl compounds or their corresponding iminium salts with active methylene compounds a series of new methine dyes with long-wavelength absorption in the near-infrared spectral range were prepared.

Keywords: active methylene compounds; (hetero)aromatic aldehydes; Knoevenagel condensation; methine dyes; NIR absorption.

1 Introduction

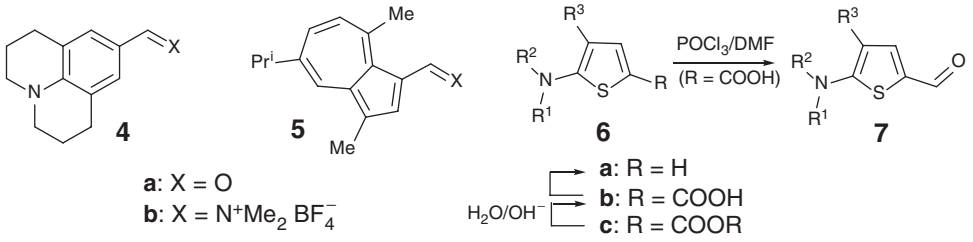
In recent years, a large variety of dyes of the general structure **D-A**, in which **D** represents a strong electron donor and **A** a strong electron acceptor moiety, have been prepared and used for different kinds of applications. For instance, such dyes have been used for determination of the solvent polarity [1–3], as light absorbers in organic solar cells [4, 5] or as molecular nanoprobes for biomedical imaging [6, 7]. The last application field could be opened due to the ability of the appropriate dyes to form highly fluorescent nanodots which are able to bind strongly at several biomaterials.

The synthetic methods for preparing the mentioned dyes are rather simple, using for example the Knoevenagel condensation of a donor-substituted aromatic aldehyde, such as 4-(dimethylamino)benzaldehyde (**1**), with an active methylene compound of the general structure **2**, in which one of the acceptor substituents in many cases is a cyano moiety [8].



2 Results and discussion

The simple route to the dyes **3** stimulated us to synthesise certain new **D-A** compounds by starting, instead of **1**, with a variety of aromatic and heteroaromatic aldehydes, such as julolidine-carbaldehyde (**4a**), 3-guaiazulenecarbaldehyde (**5a**), or their corresponding dimethyliminium salts **4b** and **5b** as well as few *N,N*-disubstituted 2-aminothiophene-5-carbaldehydes **7**. Whereas the aromatic aldehydes and their iminium salts **4–5** are easily available by the Vilsmeier formylation of their formyl-free precursors, the thiophenecarbaldehydes **7** are available by Vilsmeier formylation of *N,N*-disubstituted 2-aminothiophene-5-carboxylic acids **6b** which decarboxylate in the course of the formylation reaction yielding intermediate *N,N*-disubstituted 2-aminothiophenes **6a**. The 2-aminothiophene-5-carboxylic acids **6b** have been simply prepared by saponification of the corresponding *N,N*-disubstituted methyl 2-aminothiophene-5-carboxylates **6c** [9].



Active methylene compounds **2a–h** and as *N,N*-disubstituted 2-aminothiophene-5-carbaldehydes the compounds **7a–c** have been used as coupling partners for the Knoevenagel condensation. Most of the active

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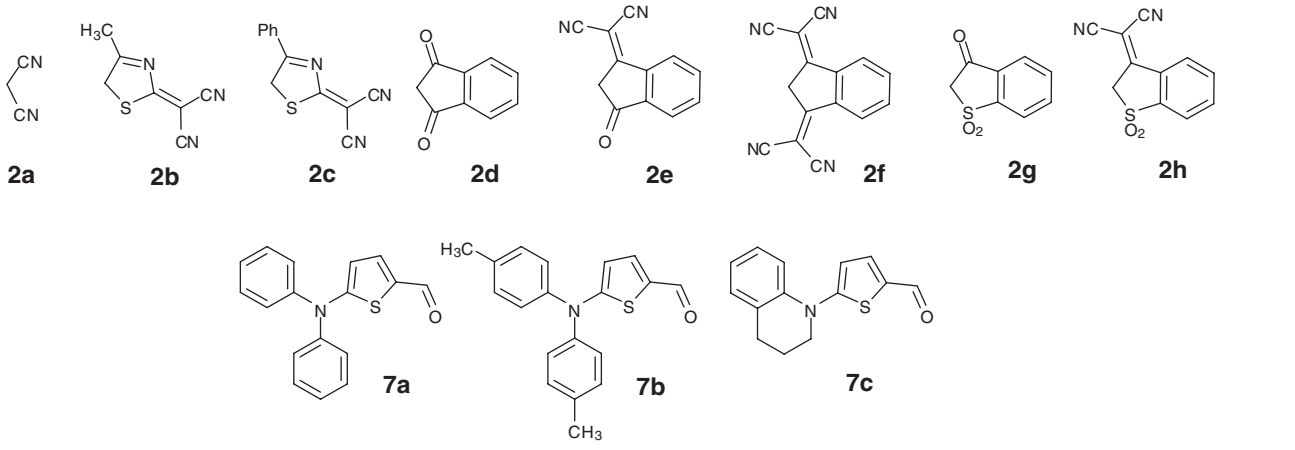
methylene compounds **2a–h** are well known and could be ordered from suited suppliers or prepared by reported methods.



By heating equimolar amounts of a compound **2** with an appropriate aldehyde **4a**, **5a** or **7a** in acetic anhydride, under consumption of the starting material, deeply coloured solutions were observed and by the time crystalline precipitates of the corresponding Knoevenagel condensation products were formed. All the products so obtained could be isolated by suction and were generally obtained subsequently in good to excellent yields.

The structures of the prepared compounds are given in the Experimental section and follow unambiguously from their analytical data. Thus, all compounds exhibit distinct mass spectra and, except for the compound **8h** build up from 2-diphenylaminothiophene-carbaldehyde (**7a**) and benzo[*b*]thiophen-3[2*H*]-one 1,1-dioxide (**2g**), characteristic ^{1}H NMR signals between $\delta \approx 7$ and 8 ppm as well as at about 9 ppm which are typical for their carbocyclic or heterocyclic moieties as well as for the methine-bonded H atoms, respectively. In the ^{1}H NMR spectrum of the compound **8h**, two sets of signals are recorded. They indicate the existence of two isomers A and B in the ratio 2:1.

In the visible spectral range, the methine dyes exhibit intense absorption bands in the red and near-infrared (NIR) spectral ranges. These absorptions are responsible for the deep blue or green colour of these compounds. Owing to their **D-A** character, the absorption maxima of these compounds exhibit, as demonstrated in Fig. 1 for the compound prepared from 2-(diphenylamino)thiophene as donor part and 2-(5-methylene-4-phenylthiazol-2(5*H*)-ylidene)malononitrile as acceptor part, a positive solvatochromism

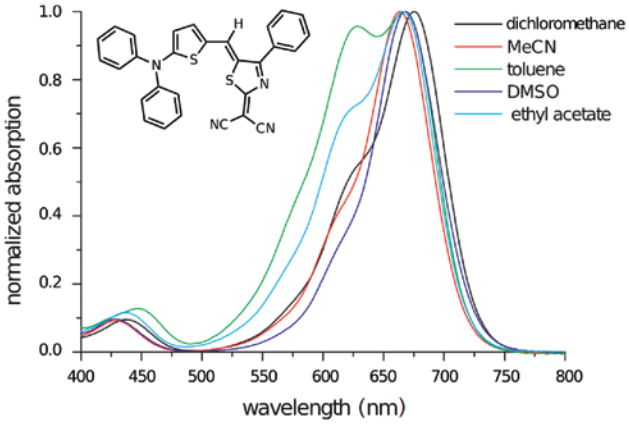


Fig. 1: Absorption spectra of a donor/acceptor dye composed of 2-diphenylaminothiophene as donor part and 2-(5-methylene-4-phenylthiazol-2(5*H*)-ylidene)malonitrile as acceptor part in different solvents.

which ranges from 629 nm in toluene up to 675 nm in dichloromethane.

3 Experimental section

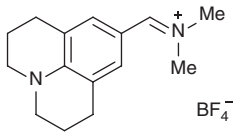
The ^{1}H NMR spectra were recorded with a Bruker DRX 500 P instrument at 500.13 MHz and the signals are recorded in Hz. The UV/Vis spectra were measured with a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer and the high-resolution mass spectra (HRMS) with a MAT 8200 Finnigan spectrometer. The melting points were estimated with a Boetius heating-table microscope.

3.1 Preparation of carbocyclic or heterocyclic iminium tetrafluoroborates (general procedure)

Phosphoryl chloride (8.43 g, 55.0 mmol) was added dropwise at 0°C under stirring within 30 min to dimethylformamide (25 mL). Stirring was continued for additional 15 min at 0°C, an aromatic or heteroaromatic compound (50.00 mmol) was added and then the reaction was allowed to defrost to ambient temperature and stirred for additional 24 h at 40°C. The resulting deep yellow solution was cooled to 0°C and then poured into ice cold water (100 mL). To isolate the desired product a 50% aqueous solution of tetrafluoroboric acid (30 mL) was added slowly under vigorous stirring. Thereby the hue of the initially deep yellow solution changed to nearly colourless and a crystalline precipitate was formed. The precipitate was filtered of by suction, washed with 0.5% aqueous tetrafluoroboric acid (10 mL) followed by water (5 mL) and dried in air.

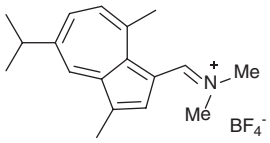
The following compounds were prepared in this way.

3.1.1 *N*-[(1,2,3,5,6,7-Hexahydropyrido[3,2,1-*ij*]quinolin-9-yl)methylene]-*N*-methylmethanaminium tetrafluoroborate (4b)



Prepared from 1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinoline hydrobromide in a yield of 97%. Yellow crystalline powder with an m.p. of 169–171°C. – ^{1}H NMR ($CDCl_3$): δ = 1.95 (quin, J = 6.0 Hz, 4 H), 2.74 (t, J = 6.0 Hz, 4 H), 3.39 (t, J = 6.0 Hz, 4 H), 3.61 (s, 3 H) 3.65 (s, 3 H), 7.31 (s, 2 H), 8.07 (s, 1 H) ppm. – HRMS ((+)-ESI): m/z = 229.16992 (calcd. 229.16990 for $[C_{15}H_{21}N_2]^+$).

3.1.2 *N*-[(5-Isopropyl-3,8-dimethylazulen-1-yl) methylene]-*N*-methylmethanaminium tetrafluoroborate (5b)



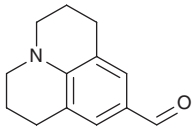
Prepared from 5-isopropyl-3,8-dimethylazulene in a yield of 98%. Brown crystalline powder with an m.p. of 155–156°C. – ^{1}H NMR ($CDCl_3$): δ = 1.39 (d, J = 7.0 Hz, 6 H), 2.56 (s, 3 H), 3.18 (s, 3 H), 3.19 (sep, J = 7.0 Hz, 1 H), 3.73 (s, 3 H), 3.78 (s, 3 H), 7.72 (d, J = 11.0 Hz, 1 H), 7.81 (dd, J = 11.0 Hz, 3.0, 1 H), 8.83 (d, J = 3.0 Hz, 1 H), 9.15 (s, 1 H) ppm. – HRMS ((+)-ESI): m/z = 254.19033 (calcd. 254.19030 for $[C_{18}H_{24}N]^+$).

3.2 Preparation of carbocyclic or heterocyclic carbaldehydes from the corresponding Vilsmeier salts (general procedure)

A slurry of the desired *N*-methyl-methanaminium tetrafluoroborate, the Vilsmeier salt (50.00 mol), in methanol (100 mL) was hydrolysed by the dropwise addition of a 5% aqueous solution of sodium hydroxide until a pH of approximately 8.0–9.0 was observed. Thereby the hue of the initially deep yellow slurry changed to nearly colourless and a crystalline precipitate was formed. The reaction solution was diluted with water (200 mL), the precipitate filtered off by suction, washed thoroughly with water until the filtrate became neutral and dried in air at room temperature.

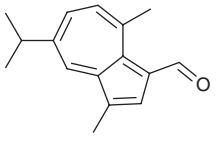
The following compounds were prepared in this way:

3.2.1 1,2,3,5,6,7-Hexahydropyrido[3,2,1-*ij*]quinoline-9-carbaldehyde (4a)



Prepared from *N*-((1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinolin-9-yl)methylene)-*N*-methyl-methanaminium tetrafluoroborate in a yield of 98%. Beige crystalline powder with an m.p. of 84°C (Lit. m.p. 83–84°C [10]. – ^{1}H NMR ($CDCl_3$): δ = 2.11 (quin, J = 6.0 Hz, 4 H), 2.84 (t, J = 6.0 Hz, 4 H), 3.33 (t, J = 6.0 Hz, 4 H), 7.37 (s, 1 H), 9.65 (s, 1 H) ppm.

3.2.2 5-Isopropyl-3,8-dimethylazulene-1-carbaldehyde (5a)



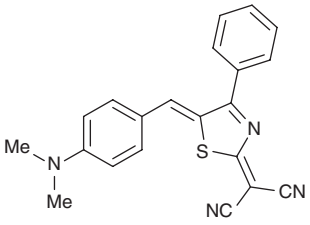
Prepared from *N*-[(5-isopropyl-3,8-dimethyazulen-1-yl) methylene]-*N*-methylmethanaminium tetrafluoroborate (**6b**) in a yield of 98%. Black crystalline powder with an m.p. of 86–87°C (Lit. m.p. 85°C [11]. – ^{1}H NMR ($CDCl_3$): δ = 1.38 (d, J = 7.0 Hz, 6 H), 2.57 (s, 3 H), 3.13 (s, 3 H), 3.16 (sep, J = 7.0 Hz, 1 H), 7.41 (d, J = 2.0 Hz, 1 H), 7.57 (d, J = 2.0 Hz, 1 H), 8.22 (s, 1 H), 8.28 (s, 1 H), 10.62 (s, 1 H) ppm.

3.3 Preparation of the methine dyes D-A (general procedure)

A mixture of an aromatic or heteroaromatic aldehyde (10.00 mmol) and an active methylene compound (10.0 mmol) in acetic anhydride (15 mL) was stirred under exclusion of moisture in a water bath at 90°C for 8 h. Under consumption of the starting material a deeply coloured solution was observed and by the time a crystalline precipitate was formed. After cooling to 0°C the precipitate was filtered off by suction, washed exhaustively with methanol (100–200 mL) until the filtrate showed the colour of the desired product in solution and then dried in air at room temperature.

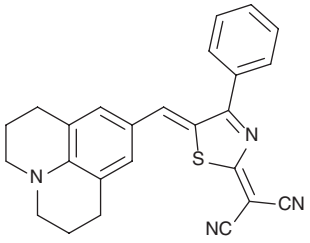
The following compounds were so prepared.

3.3.1 (*Z*)-2-{5-(4-Dimethylamino)benzylidene]-4-phenylthiazol-2(5*H*)-ylidene}malononitrile (8a)



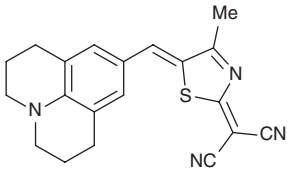
Prepared from 4-(dimethylamino)benzaldehyde (**1**) and 2-(4-phenylthiazol-2(5*H*)-ylidene)malononitrile (**2c**) [12] in a yield of 91%. Green crystalline powder with golden lustre and an m.p. of 295–296°C (dec.). – UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 630 nm (4.85). – ^{1}H NMR ($CDCl_3$): δ = 3.18 (s, 6 H), 6.76 (d, J = 9.0 Hz, 2 H), 7.55 (t, J = 7.5 Hz, 2 H), 7.56 (d, J = 9.0 Hz, 2 H), 7.59 (s, 1 H), 7.61 (t, J = 7.5 Hz, 1 H), 7.77 (d, J = 7.5 Hz, 2 H) ppm. – HRMS ((+)-ESI): m/z = 356.10939 (calcd. 356.10952 for $[C_{21}H_{16}N_4S]^+$).

3.3.2 (*Z*)-2-{5-[(1,2,3,5,6,7-Hexahydropyrido[3,2,1-*ij*] quinolin-9-yl)methylene]-4-phenylthiazol-2(5*H*)-ylidene}malononitrile (8b)



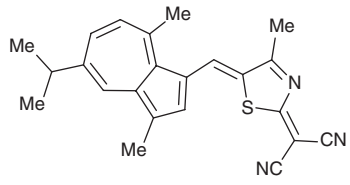
Prepared from 1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinoline-9-carbaldehyde (**4a**) and 2-(4-phenylthiazol-2(5*H*)-ylidene)malononitrile (**2c**) [12] in a yield of 97%. Dark green crystalline powder with an m.p. of 217–218°C (dec.). – UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 664 nm (5.05). – ^{1}H NMR ($CDCl_3$): δ = 2.00 (t, J = 6.0, 4 H), 2.72 (t, J = 6.0 Hz, 4 H), 3.43 (t, J = 6.0 Hz, 4 H), 7.07 (s, 2 H), 7.49 (s, 1 H), 7.53 (t, J = 7.5 Hz, 2 H), 7.57 (t, J = 7.5 Hz, 1 H), 8.50 (d, J = 7.5 Hz, 2 H) ppm. – HRMS ((+)-ESI): m/z = 408.13622 (calcd. 408.14088 for $[C_{25}H_{20}N_4S]^+$).

3.3.3 2-{4-Methyl-5-[(2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinolin-9-yl)methylene]thiazol-2(5*H*)-ylidene}malononitrile (8c)



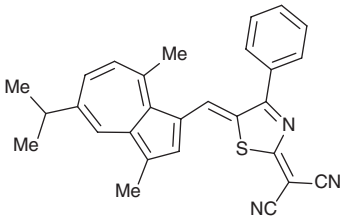
Prepared from 1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinoline-9-carbaldehyde (**4a**) and 2-(4-methylthiazol-2(5*H*)-ylidene)malononitrile (**2b**) [12] in a yield of 97%. Green crystalline powder with golden lustre and an m.p. of 209–211°C (dec.). – UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 659 nm (5.04). – ^{1}H NMR ($CDCl_3$): δ = 1.90 (t, J = 6.0 Hz, 4 H), 2.75 (t, J = 6.0 Hz, 4 H), 3.17 (s, 3 H), 3.46 (t, J = 6.0 Hz, 4 H), 7.32 (s, 2 H), 8.00 (s, 1 H) ppm. – HRMS ((+)-ESI): m/z = 346.12697 (calcd. 346.12527 for $[C_{20}H_{18}N_4S]^+$).

3.3.4 2-{5-[(5-Isopropyl-3,8-dimethylazulen-1-yl)methylene]-4-methylthiazol-2(5*H*)-ylidene}malononitrile (8d)



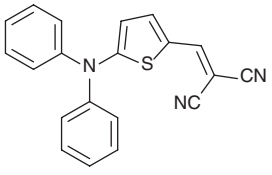
Prepared from 5-isopropyl-3,6-dimethylazulene-1-carbaldehyde (**5a**) and 2-(4-methylthiazol-2(5*H*)-ylidene) malononitrile (**2b**) [12] in a yield of 98%. Dark green crystalline powder with an m.p. of 273–274°C (dec.). – UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 675 (4.83), 633 nm (4.75). – ^{1}H NMR ($CDCl_3$): δ = 1.40 (d, J = 7.0 Hz, 6 H), 2.63 (s, 3 H), 2.68 (s, 3 H), 3.18 (sep, J = 7.0 Hz, 1 H), 3.20 (s, 3 H), 7.49 (d, J = 11.0 Hz, 1 H), 7.67 (dd, J = 11.0 Hz, 2.0, 1 H), 8.04 (s, 1 H), 8.25 (d, J = 2.0 Hz, 1 H), 8.61 (s, 1 H) ppm. – HRMS ((+)-ESI): m/z = 371.14617 (calcd. 371.14562 for $[C_{23}H_{21}N_3S]^+$).

3.3.5 2-{5-[(5-Isopropyl-3,8-dimethylazulen-1-yl)methylene]-4-phenylthiazol-2(5*H*)-ylidene}malononitrile (8e)



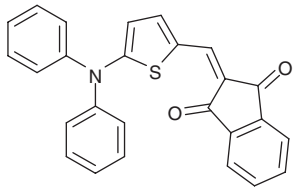
Prepared from 5-isopropyl-3,6-dimethylazulene-1-carbaldehyde (**5a**) and 2-(4-phenylthiazol-2(5*H*)-ylidene) malononitrile (**2c**) [12] in a yield of 98%. Green crystalline powder with golden lustre and an m.p. of 271°C (dec.). – UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 696 (4.86), 652 (4.75). – ^{1}H NMR ($CDCl_3$): δ = 1.39 (d, J = 7.0 Hz, 6 H), 2.62 (s, 3 H), 2.87 (s, 3 H), 3.18 (sep, J = 7.0 Hz, 1 H), 7.44 (d, J = 11.0 Hz, 1 H), 7.54 (t, J = 7.0 Hz, 2 H), 7.59 (t, J = 7.0 Hz, 1 H), 7.66 (d, J = 11.0 HZ, 1 H), 7.77 (d, J = 7.0 Hz, 2 H), 8.09 (s, 1 H), 8.25 (s, 1 H), 8.65 (s, 1 H) ppm. – HRMS ((+)-ESI): m/z = 433.16172 (calcd. 433.16130 for $[C_{28}H_{23}N_3S]^+$).

3.3.6 2-{[5-(Diphenylamino)thiophen-2-yl] methylene}malononitrile (8f)



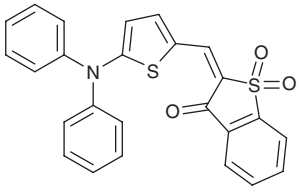
Prepared from 5-(diphenylamino)thiophene-2-carbaldehyde (**7a**) [9] and malononitrile (**2a**) in a yield of 69%. Orange crystals with an m.p. of 190–191°C. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 472 nm (4.73). ^{1}H NMR ([D_6]DMSO): δ = 6.34 (d, J = 4.5 Hz, 1 H), 7.38 (t, J = 7.5 Hz, 2 H), 7.45 (d, J = 7.5 Hz, 4 H), 7.51 (t, J = 7.5 Hz, 4 H), 7.70 (d, J = 4.5 Hz, 1 H), 8.22 (s, 1 H) ppm. – HRMS ((+)-ESI): m/z = 327.08347 (calcd. 327.08308 for $[C_{20}H_{13}N_3S]^+$).

3.3.7 2-{[5-(Diphenylamino)thiophen-2-yl]methylen})-1*H*-indene-1,3(2*H*)-dione (8g)



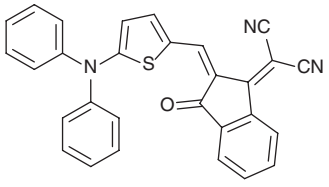
Prepared from 5-(diphenylamino)thiophene-2-carbaldehyde (**7a**) [9] and 1*H*-indene-1,3(2*H*)-dione (**2d**) in a yield of 86%. Brownish-red crystals with an m.p. of 298–299°C. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 519 nm (4.88). – ^{1}H NMR ($CDCl_3$): δ = 6.44 (d, J = 4.5 Hz, 1 H), 7.29 (t, J = 7.5 Hz, 2 H), 7.34 (d, J = 7.5 Hz, 4 H), 7.41 (t, J = 7.5 Hz, 4 H), 7.64 (d, J = 4.5 Hz, 1 H), 7.65 (m, 2 H), 7.77 (m, 1 H), 7.78 (s, 1 H), 7.83 (m, 1 H) ppm. – HRMS ((+)-ESI): m/z = 407.09803 (calcd. 407.09803 for $[C_{26}H_{17}NO_2S]^+$).

3.3.8 (*E*,*Z*)-2-{[5-(Diphenylamino)thiophen-2-yl] methylene}-benzo[*b*]thiophen-3[2*H*]-one 1,1-dioxide (8h)



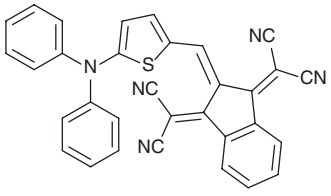
Prepared from 5-(diphenylamino)thiophene-2-carbaldehyde **7a** [9] and benzo[*b*]thiophen-3[2*H*]-one 1,1-dioxide (**2g**) [13] in a yield of 92% as a mixture of two isomers. Pinkish red crystalline powder with an m.p. of 283°C. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 521 nm (4.83). – ^{1}H NMR ($CDCl_3$): δ = 6.44 (d, J = 4.5 Hz, 1 H, isomer A), 6.47 (d, J = 4.5 Hz, 1 H, isomer B), 7.29 (dt, J = 7.5 Hz, 1.5 Hz, 2 H, isomer A), 7.31 (dt, J = 7.5 Hz, 1.5 Hz, 2 H, isomer B), 7.33 (dd, J = 7.5 Hz, 1.0 Hz, 4 H, isomer A), 7.35 (dd, J = 7.5 Hz, 1.0 Hz, 4 H, isomer B), 7.41 (dt, J = 7.5 Hz, 2.0 Hz, 4 H, isomer A), 7.43 (dt, J = 7.5 Hz, 2.0 Hz, 4 H, isomer B), 7.62 (s, broad, 1 H, isomer B), 7.64 (s, broad, 1H, isomer A), 7.68 (td, J = 7.5 Hz, 1.0 Hz, 1 H, isomer B), 7.73 (td, J = 7.5 Hz, 1.0 Hz, 1 H, isomer A), 7.74 (td, J = 7.5 Hz, 1.0 Hz, 1 H, isomer B), 7.78 (td, J = 7.5 Hz, 1.0 Hz, 1 H, isomer A), 7.83 (s, broad, 1 H, isomer B), 7.85 (s, broad, 1 H, isomer A), 7.89 (dt, J = 7.5 Hz, 1.0 Hz, 1 H, isomer B), 7.91 (dt, J = 7.5 Hz, 1.0 Hz, 1 H, isomer B), 7.92 (dt, J = 7.5 Hz, 1.0 Hz, 1 H, isomer A), 8.00 (dt, J = 7.5 Hz, 1.0 Hz, 1 H, isomer A) ppm. – HRMS ((+)-ESI): m/z = 443.06442 (calcd. 443.06492 for $[C_{25}H_{17}NO_3S]^+$).

3.3.9 2-{2-[(5-Diphenylaminothiophen-2-yl) methylene]-3-oxo-2,3-dihydro-1*H*-indene-1-ylidene}malononitrile (8i)



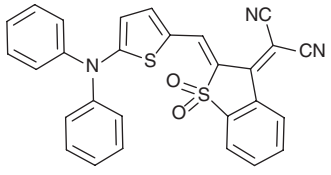
Prepared from 5-(diphenylamino)thiophene-2-carbaldehyde (**7a**) [9] and 2-(3-oxo-2,3-dihydro-1*H*-inden-1-ylidene) malononitrile (**2e**) [14] in a yield of 84%. Brownish-green crystals with golden lustre and an m.p. of 265–266°C. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 591 nm (4.85). – ^{1}H NMR ($CDCl_3$): δ = 6.46 (d, J = 4.5 Hz, 1 H), 7.30 (t, J = 7.5 Hz, 2 H), 7.37 (d, J = 7.5 Hz, 4 H), 7.46 (t, J = 7.5 Hz, 4 H), 7.57 (t, J = 7.5 Hz, 1 H), 7.61 (m, 2 H), 7.70 (d, J = 7.5 Hz, 1 H), 8.56 (d, J = 7.5 Hz, 1 H), 8.66 (s, 1 H) ppm. – HRMS ((+)-ESI): *m/z* = 455.11009 (calcd. 455.10931 for $[C_{29}H_{17}N_3OS]^+$).

3.3.10 2,2′-{2-[(5-(Diphenylamino)thiophen-2-yl)methylene]-1*H*-indene-1,3(2*H*)-diylidene}dimalononitrile (8j)



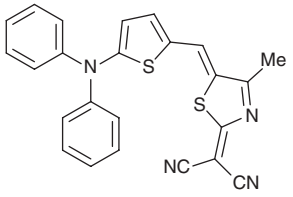
Prepared from 5-(diphenylamino)thiophene-2-carbaldehyde (**7a**) [9] and 2,2′-(1*H*-indene-1,3(2*H*)-diylidene) dimalononitrile (**2f**) [15] in a yield of 94%. Deep blue crystalline powder with an m.p. of 229–230°C. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 666 nm (4.59). – ^{1}H NMR ($CDCl_3$): δ = 6.44 (s, broad), 7.38 (d, J = 7.5 Hz, 4 H), 7.42 (t, J = 7.5 Hz, 2 H), 7.50 (t, J = 7.5 Hz, 4 H), 7.56 (t, J = 5.5 Hz, 1 H), 7.58 (t, J = 5.5 Hz, 1 H), 7.65 (d, J = 5.0 Hz, 1 H), 8.42 (d, J = 5.5 Hz, 1 H), 8.43 (d, J = 5.5 Hz, 1 H), 8.65 (s, broad, 1 H) ppm. – HRMS ((+)-ESI): *m/z* = 503.12051 (calcd. 503.12019 for $[C_{32}H_{17}N_5S]^+$).

3.3.11 2-{2-[(5-Diphenylaminothiophen-2-yl) methylene]-1,1-dioxidobenzo[*b*]thiophen-3(2*H*)-ylidene}malononitrile (8k)



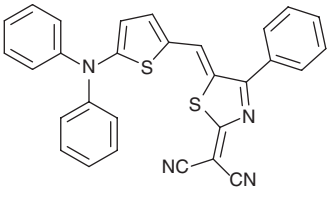
Prepared from 5-(diphenylamino)thiophene-2-carbaldehyde (**7a**) [9] and 2-(1,1-dioxobenzo[*b*]thiophen-3(2*H*) ylidene)malononitrile (**2h**) [16] in a yield of 92%. Green crystals with golden lustre and an m.p. of 258–260°C. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 624 nm (4.93). – ^{1}H NMR ([D_6]DMSO): δ = 6.54 (d, J = 4.5 Hz, 1 H), 7.48 (t, J = 7.5 Hz, 2 H), 7.58 (t, J = 7.5 Hz, 4 H), 7.63 (d, J = 7.5 Hz, 4 H), 7.90 (t, J = 7.5 Hz, 1 H), 7.94 (t, J = 7.5 Hz, 1 H), 7.96 (d, J = 4.5 Hz, 1 H), 8.05 (d, J = 7.5 Hz, 1 H), 8.49 (s, 1 H), 8.60 (d, J = 7.5 Hz, 1 H) ppm. – HRMS ((+)-ESI): *m/z* = 91.07655 (calcd. 419.07616 for $[C_{26}H_{17}N_3O_2S_2]^+$).

3.3.12 2-{2-[(5-Diphenylaminothiophen-2-yl) methylene]-4-methylylthiazol-2(5*H*)-ylidene}-malononitrile (8l)



Prepared from 5-(diphenylamino)thiophene-2-carbaldehyde (**7a**) [9] and 2-(4-methylthiazol-2(5*H*)-ylidene)malononitrile (**2b**) [12] in a yield of 94%. Green crystals with golden lustre and an m.p. of 225°C. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 655 nm (4.90). – ^{1}H NMR (CD_2Cl_2): δ = 2.59 (s, 3 H), 6.50 (d, J = 4.5 Hz, 1 H), 7.35–7.38 (m, 6 H), 7.46–7.49 (m, 5 H), 7.71 (s, 1 H) ppm. – HRMS ((+)-ESI): *m/z* = 424.08255 (calcd. 424.08167 for $[C_{24}H_{16}N_4S_2]^+$).

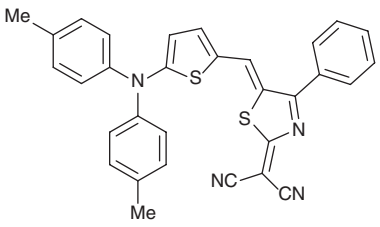
3.3.13 2-{2-[(5-Diphenylaminothiophen-2-yl) methylene]-4-phenylthiazol-2(5*H*)-ylidene}malononitrile (8m)



Prepared from 5-(diphenylamino)thiophene-2-carbaldehyde (**7a**) [9] and 2-(4-phenylthiazol-2(5*H*)-ylidene)malononitrile (**2c**) [12] in a yield of 91%. Green crystals with golden lustre and an m.p. of 308°C. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 675 nm (4.94). – ^{1}H NMR ($CDCl_3$): δ = 6.47 (d, J = 4.5 Hz, 1 H), 7.31 (t, J = 7.0 Hz, 2 H), 7.34 (d, J = 7.0 Hz, 4 H), 7.38 (d, J = 4.5 Hz, 1 H), 7.40 (t, J = 8.5 Hz, 4 H), 7.51 (t,

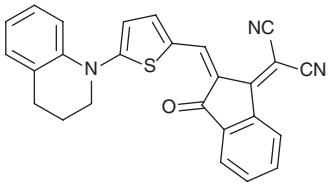
J = 7.5 Hz, 2 H), 7.57 (t, *J* = 7.5 Hz, 1 H), 7.69 (s, 1 H), 7.70 (d, *J* = 7.5 Hz, 2 H) ppm. – HRMS ((+)-ESI): *m/z* = 486.09700 (calcd. 486.09734 for $[C_{29}H_{18}N_4S_2]^+$).

3.3.14 2-{5-[(5,5-(Di-*p*-tolylamino)thiophen-2-yl)methylene]-4-phenylthiazol-2(5*H*)-ylidene}malononitrile (8n)



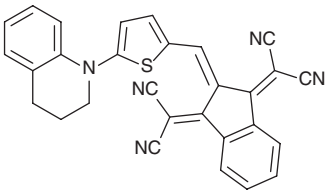
Prepared from 5-(di-*p*-tolylamino)thiophene-2-carbaldehyde (**7b**) [9] and 2-(4-phenylthiazol-2(5*H*)-ylidene)malononitrile **(2c**) [12] in a yield of 93%. Green crystals with golden lustre and an m.p. of 306°C. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 680 nm (4.96). – ^{1}H NMR ($CDCl_3$): δ = 2.35 (s, 6 H), 6.42 (d, *J* = 4.5 Hz, 1 H), 7.13 (d, *J* = 8.5 Hz, 4 H), 7.21 (d, *J* = 8.5 Hz, 4 H), 7.38 (d, *J* = 4.5 Hz, 1 H), 7.51 (t, *J* = 7.5 Hz, 2 H), 7.56 (t, *J* = 7.5 Hz, 1 H), 7.70 (s, 1 H), 7.71 (d, *J* = 7.5 Hz, 2 H) ppm. – HRMS ((+)-ESI): *m/z* = 514.12785 (calcd. 514.12868 for $[C_{31}H_{22}N_4S_2]^+$).

3.3.15 (*Z*)-2-{2-[(5-(3,4-Dihydroquinolin-1(2*H*)thiophen-2-yl)methylene]3-oxo-2,3-dihydro-1*H*-inden-1-ylidene}malononitrile (8o)



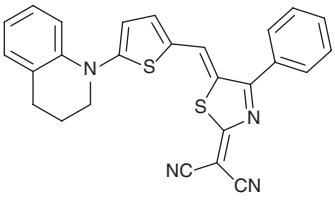
Prepared from 5-(3,4-dihydroquinolin-1(2*H*)-yl)thiophene-2-carbaldehyde (**7c**) [9] and 2-(3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (**2e**) [14] in a yield of 88%. Dark green spicular crystals with an m.p. of 215°C. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 596 nm (4.98). – ^{1}H NMR (CD_2Cl_2): δ = 2.12 (quin, *J* = 6.5 Hz, 2 H), 2.79 (t, *J* = 6.5 Hz, 2 H), 3.94 (t, *J* = 6.5 Hz, 2 H), 6.86 (d, *J* = 5.0 Hz, 1 H), 7.19 (t, *J* = 7.5 Hz, 1 H), 7.26 (d, *J* = 7.5 Hz, 1 H), 7.31 (t, *J* = 7.5 Hz, 1 H), 7.75–7.65 (m, 4 H), 7.71 (d, *J* = 7.5 Hz, 1 H), 8.52 (d, *J* = 7.5 Hz, 1 H), 8.61 (s, 1 H) ppm. – HRMS ((+)-ESI): *m/z* = 419.10997 (calcd. 419.10915 for $[C_{26}H_{17}N_3SO]^+$).

3.3.16 2,2′-{2-[5-(3,4-Dihydroquinolin-1(2*H*) thiophen-2-yl)methylene]-1*H*-inden-1,3(2*H*)-diylidene}dimalononitrile (8p)



Prepared from 5-(3,4-dihydroquinolin-1(2*H*)-yl)thiophene-2-carbaldehyde (**7c**) [9] and 2,2′-(1*H*-indene-1,3(2*H*)-diylidene)dimalononitrile (**2f**) [15] in a yield of 83%. Deep blue crystalline powder with an m.p. of 246°C (dec.). – UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 672 nm (4.60). – ^{1}H NMR ($CDCl_3$): δ = 2.18 (quin, *J* = 6.5 Hz, 2 H), 2.84 (t, *J* = 6.5 Hz, 2 H), 3.93 (t, *J* = 6.5 Hz, 2 H), 6.83 (s, broad, 1 H), 7.26 (d, *J* = 7.5 Hz, 1 H), 7.28 (t, *J* = 7.5 Hz, 1 H), 7.33 (t, *J* = 7.5 Hz, 1 H), 7.56 (d, *J* = 7.5 Hz, 1 H), 7.57 (t, *J* = 6.5 Hz, 1 H), 7.60 (t, *J* = 6.5 Hz, 1 H), 7.73 (d, *J* = 5.0 Hz, 1 H), 8.47 (d, *J* = 6.5 Hz, 1 H), 8.57 (d, *J* = 6.5 Hz, 1 H), 8.69 (s, broad, 1 H) ppm. – HRMS ((+)-ESI): *m/z* = 467.12087 (calcd. 467.12050 for $[C_{29}H_{17}N_5S]^+$).

3.3.17 2-{5-[5-(3,4-Dihydroquinolin-1(2*H*)-yl)thiophen-2-yl)methylene]-4-phenylthiazol-2(5*H*)-ylidene}malononitrile (8q)



Prepared from 5-(3,4-dihydroquinolin-1(2*H*)-yl)thiophene-2-carbaldehyde (**7c**) [9] and 2-(4-phenylthiazol-2(5*H*)-ylidene)malononitrile **2c** [12] in a yield of 83%. Green crystals with golden lustre and an m.p. of 254°C. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 682 nm (5.00). – ^{1}H NMR ($CDCl_3$, CF_3COOH): δ = 2.30 (quin, *J* = 6.5 Hz, 2 H), 2.94 (t, *J* = 6.5 Hz, 2 H), 4.28 (t, *J* = 6.5 Hz, 2 H), 7.36 (d, *J* = 5.5 Hz, 1 H), 7.40–7.49 (m, 4 H), 7.52 (d, *J* = 7.5 Hz, 2 H), 7.58 (t, *J* = 7.5 Hz, 2 H), 7.68 (t, *J* = 7.5 Hz, 1 H), 7.76 (s, 1 H), 7.86 (d, *J* = 5.5, 1 H) ppm. *J* = 6.5 Hz, 1 H), 8.57 (d, *J* = 6.5 Hz, 1 H), 8.69 (s, broad, 1 H) ppm. – HRMS ((+)-ESI): *m/z* = 455.09750 (calcd. 455.09736 for $[C_{26}H_{16}N_4S_2]^+$).

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