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TETRAHEDRON

The New and Simple 'LEGO' System: Synthesis and Reactions of Thienyl-Substituted 4-Tributylstannyl-2,6-Oligopyridines

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Dedicated to Prof. Dr. Reiner Sustmann on the occasion of his 60th birthday.

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Abstract

3,5-Disubstituted 1,2,4-triazines **3** are converted regioselectively to 4-tributylstannyl-2,6-oligopyridines **4** via [4+2] cycloadditions with ethynyltributyltin. These tin compounds **4** are coupled with aryl bromides and aryloyl chlorides in palladium catalyzed reactions to 4-aryl-2,6-oligopyridines and 4-aryloyl-2,6-oligopyridines **6**.

Keywords: *Triazines; Pyridines; Tin and compounds; Coupling reactions*

INTRODUCTION

In this communication we extend our new 'LEGO' system [1-7], a new and simple high yield route to pyridines via 1,2,4-triazines, to the generation of 4-tributylstannyl-, 4-aryl- and 4-aryloyl-2,6-oligopyridines with oligothienyl substituents (Scheme 1).

The central point of our strategy is the regiospecific condensation of carboxamidrazones **1** (Table 1) with thienylglyoxals **2** (Table 1) to form 3,5-disubstituted 1,2,4-triazines **3** (Table 2) [4] which can be transformed either to 2,6-oligopyridines via inverse-type Diels-Alder reactions with norborna-2,5-diene as a synthetic equivalent for acetylene (Scheme 1, route A) [1-5] or to 4-tributylstannyl-2,6-oligopyridines **4** via inverse-type Diels-Alder reactions with ethynyltributyltin (Scheme 1, route B) [6,7]. The reaction sequence described offers a simple and high yield access to the formerly unknown 4-tributylstannyl-2,6-oligopyridines **4**.

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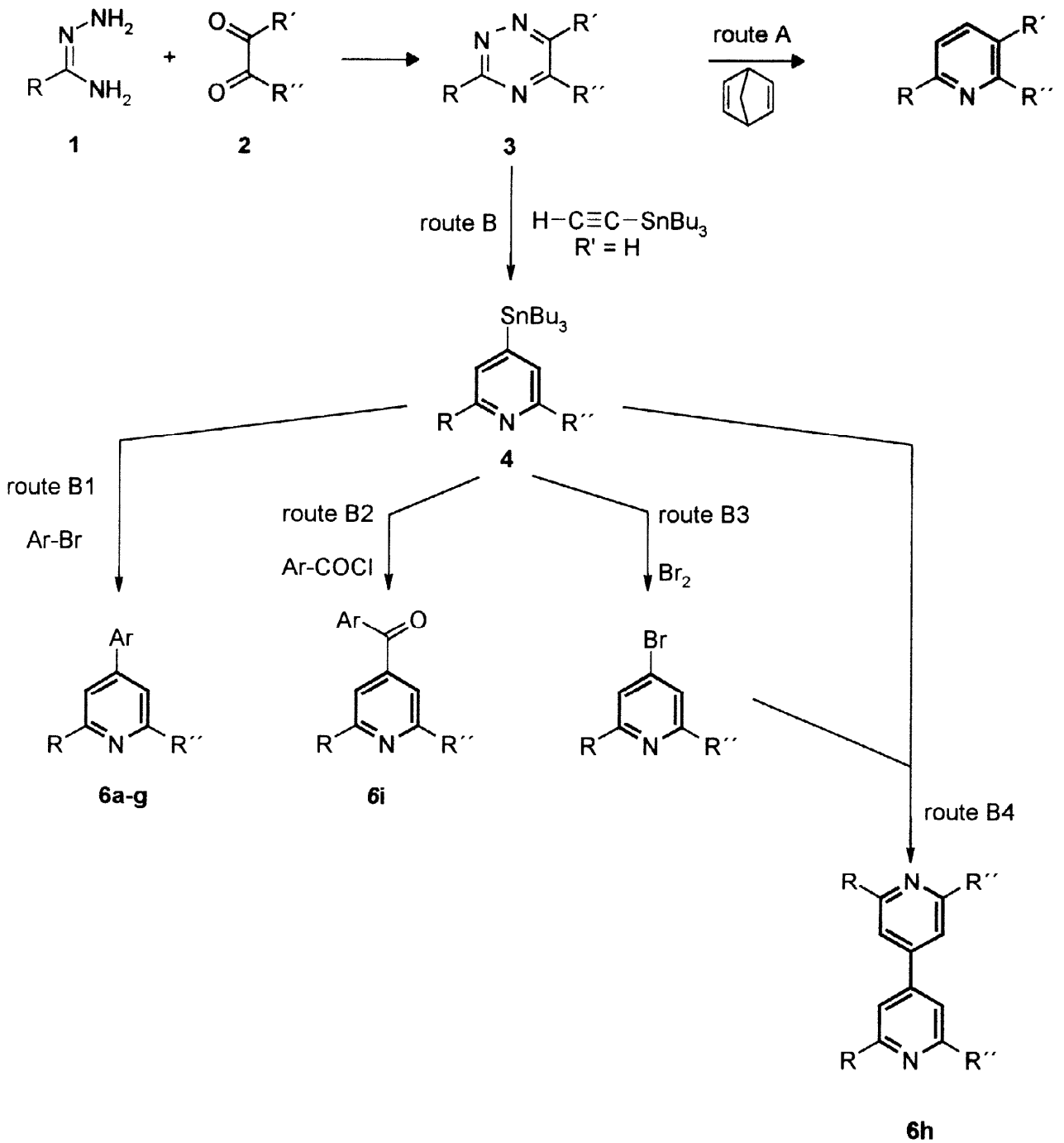
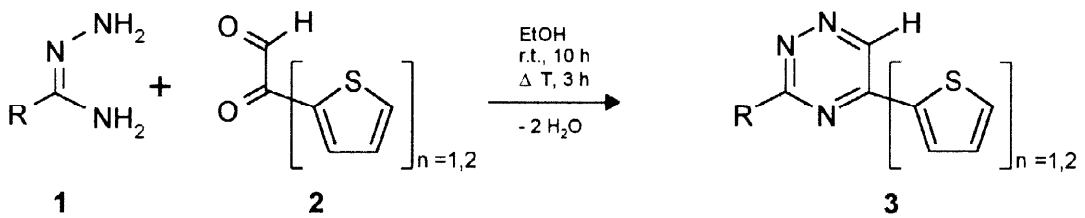
The chemistry of organotin compounds has been extensively investigated [8,9]. We used Stille cross-coupling reactions [10,11] (Scheme 1, route B1 and route B2) and electrophilic ipso substitutions (Scheme 1, route B3) for further derivatizations of the tributyltin compounds **4**. Finally, complex heterocyclic chains **6** can be obtained by coupling brominated pyridines with 4-tributyltin-2,6-oligopyridines **4** (Scheme 1, route B4) [6].



Scheme 1. The new and simple 'LEGO' System. Pyridine rings resulting from triazine rings in extra bold print.

RESULTS AND DISCUSSION

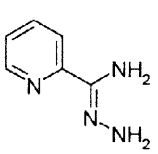
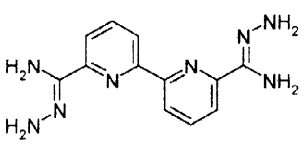
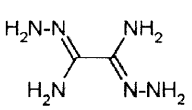
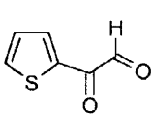
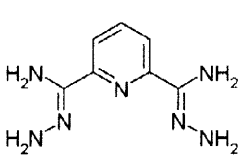
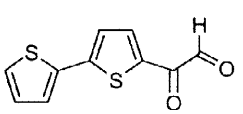
Synthesis of 1,2,4-triazines: 1,2,4-Triazines are easily prepared by cyclocondensation of carboxamidrazones with 1,2-dicarbonyl compounds [12]. Unsymmetrically substituted 1,2-diones, such as α-arylglyoxals, lead to 3,5-disubstituted 1,2,4-triazines [1,4,13,14] regioselectively, a fact which considerably simplifies workup procedures and raises yields. The regioselectivity is proved by the ^{1}H NMR spectra of 1,2,4-triazines **3**, exhibiting in each case just one singlet for the expected triazine H^6. Furthermore, the structure of the corresponding pyridines obtained from these 1,2,4-triazines is confirmed by the expected coupling constants for 4-substituted 2,6-oligopyridines. We restricted our synthetic investigations to a small selection of 3,5-disubstituted 1,2,4-triazines, which have already offered a considerable number of possible combinations of carboxamidrazone with α-arylglyoxals.



Scheme 2. Synthesis of 3,5-disubstituted 1,2,4-triazines

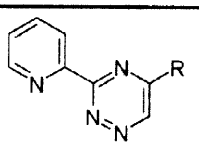
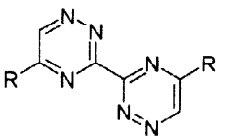
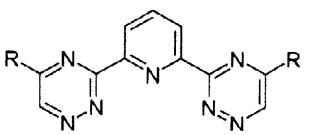
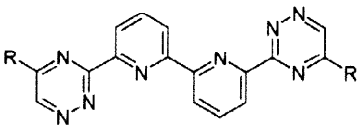
Reactions (Scheme 2) affording 1,2,4-triazines (Table 2) were carried out in ethanol as solvent at ambient temperature for 10 h, followed by heating to reflux for 3h.

Table 1. Starting compounds for synthesis of 1,2,4-triazines according to scheme 2: Amidrazones and glyoxals.

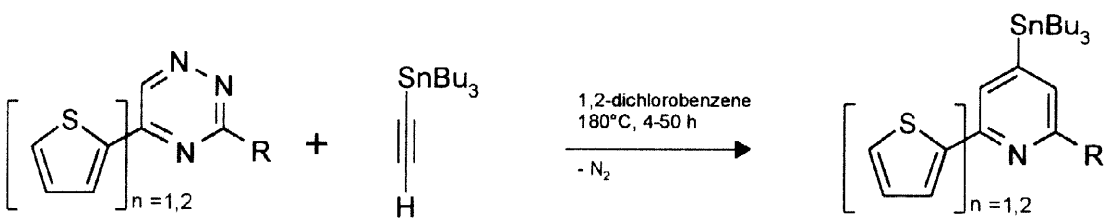
Compound		Ref.	Compound		Ref.
1a		[15]	**1d**		--
1b		[16]	**2a**		[18]
1c		[17]	**2b**		[19]

The only problem we encountered in this step was the availability of the carboxamidrazones, which are only accessible for electron withdrawing substituents like pyridine. Hence, all efforts to synthesize thienyl-carboxamidrazones were unsuccessful.

Table 2. Mono-, bi- and bis-1,2,4-triazines, obtained from amidrazones **1** and thienylglyoxals **2**.

Amidrazone	Glyoxal	Triazine [Ref.]		R	Yield [%]	M.P. [°C]
1a	**2b**	**3a** [4]		[2,2′]-bithiophen-5-yl	64	179-181
1b	**2a**	**3b**		thiophen-2-yl	79	245-247
1b	**2b**	**3c**		[2,2′]-bithiophen-5-yl	97	280-283
1c	**2a**	**3d**		thiophen-2-yl	87	261-263
1c	**2b**	**3e**		[2,2′]-bithiophen-5-yl	81	283-285
1d	**2a**	**3f**		thiophen-2-yl	84	303-306

Synthesis of stannylated pyridines from 1,2,4-triazines: 1,2,4-Triazines are known to undergo inverse type Diels-Alder reactions with angle-strained and electron rich dienophiles to yield dihydropyridines and pyridines after extrusion of nitrogen [1-7,12]. The reaction with ethynyltributyltin as dienophile affording stannylated pyridines was first investigated systematically in our laboratories [6,7]. Compared to 1,2,4,5-tetrazines, 1,2,4-triazines possess lower reactivity in [4+2] cycloaddition reactions [20], therefore, high reaction temperatures are necessary to supply the activation energy. We used 1,2-dichlorobenzene as solvent which turned out to be the solvent of choice concerning yields and reaction times. The reactions afforded the 4-stannylated pyridines **4** as major isomers because of steric reasons (Scheme 3, Table 3).

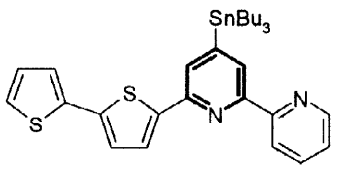
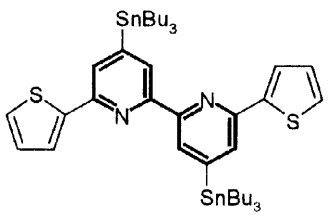
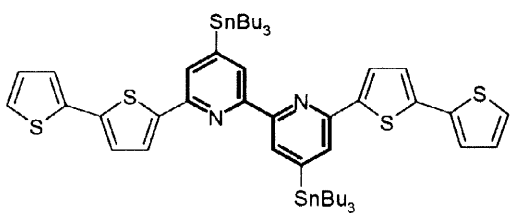
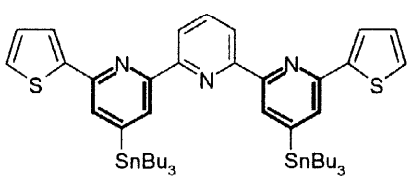
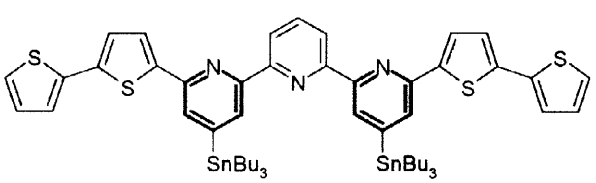
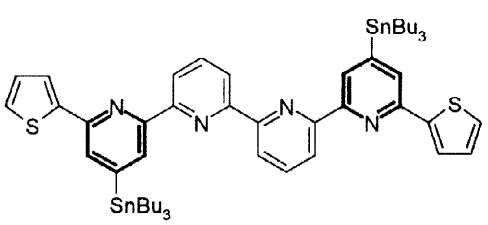


3 **4**

Scheme 3. Synthesis of 4-stannylated pyridines

In 4-position the steric hindrance for the tributyltin group is smaller than in 3-position in the transition state. Except for compound **4a**, the isolation and characterization of the minor amount of 3-stannylated isomers were not possible.

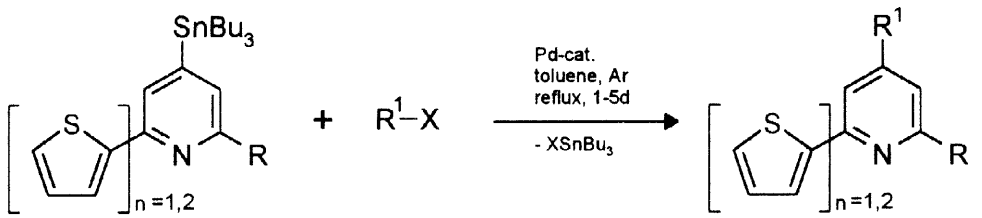
Table 3. Synthesis of 4-tributylstannyl-pyridines **4** according to Scheme 3.

Triazine	4-Tributylstannyl-pyridine	Reaction times and Conditions	Yield [%]	M.P. [°C]
3a	**4a** 	175°C, 20h	46	oil
3b	**4b** 	180°C, 4h	74	oil
3c	**4c** 	180°C, 32h	64	51-52
3d	**4d** 	185°C, 12h	58	53-55
3e	**4e** 	180°C, 50h	43	40-41
3f	**4f** 	185°C, 44h	34	115-117

Due to the stability of the C-Sn bond (bond energy 50 kcal/mol), stannylated pyridines are neither air sensitive nor water sensitive and therefore they can be stored for months without

decomposition. Because of their good solubility in organic solvents they can be purified chromatographically.

Pd-catalyzed cross-coupling reactions: In the last years a new type of generating carbon-carbon bonds was found in the palladium catalyzed cross-coupling reaction of stannylated compounds with organic halides or related compounds [8-10]. Up to now it has not been possible to introduce electrophiles in 4-position of the pyridine ring directly.



4 **5** **6**

Scheme 4. Cross-coupling reactions with aryl- and acyl-halides (X= Cl, Br).

Stille cross-coupling reactions of stannylated compounds **4** with aryl- or acyl-halides **5** (Table 4) offer an elegant approach to 4-arylated and acylated pyridines **6** (Scheme 4, Table 5). Until now we have only used the "workhorse" catalyst $Pd(PPh_3)_4$ for arylations in toluene as solvent and $BnPdCl(PPh_3)_2$ for acylations in chloroform as solvent.

Table 4. Aryl bromides and acyl chloride according to Scheme 4.

R^1-X		R^1-X	
5a	2-bromo-thiophene	**5d**	9-bromo-anthracene
5b	2-bromo-5-octan-1-yl-thiophene	**5e**	4-bromo-[2,2']-bipyridine
5c	5-bromo-[2,2',5',2'']-terthiophene	**5f**	4-octadecyl-benzoyl chloride

The reactions proceeded with S and N heterocycles, although heterocycles containing nitrogen are reported to form complexes with the catalyst and thus inhibiting the reaction [21]. Generally, the solubility of oligopyridines **6** decreases with increasing chain length. Melting points of these compounds are indirectly proportional to their solubility: a higher melting point means lower solubility. Alkyl chains were introduced to improve the solubility of the coupling products **6**. Thus, solubility of compound **6e** in dichloromethane is increased about 100 times compared to that of compound **6c**. Furthermore, introduction of alkyl chains may lead to liquid-crystal properties. Unfortunately the phase-transitions were not reversible according to DSC measurements.

Table 5a. Synthesis of 4-thienyl-pyridines **4** according to Scheme 4.

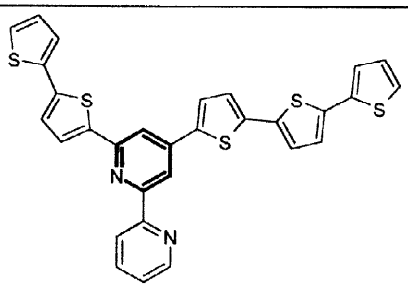
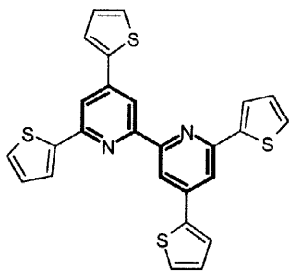
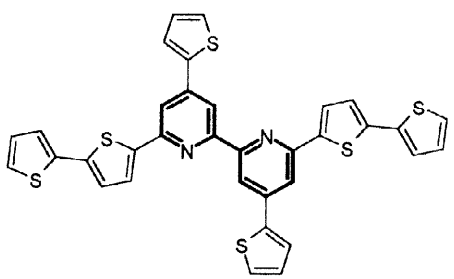
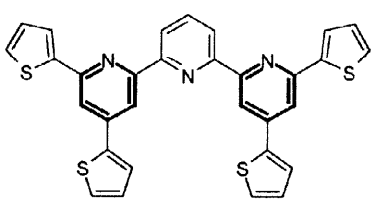
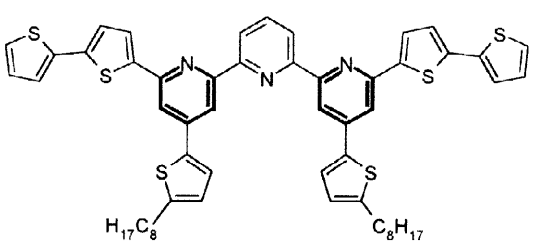
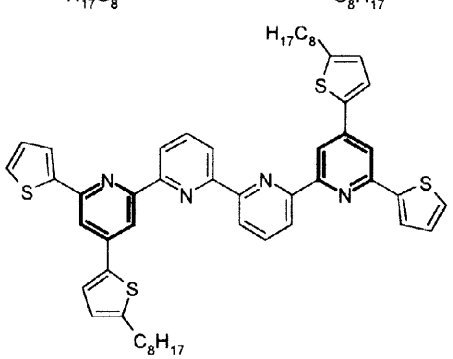
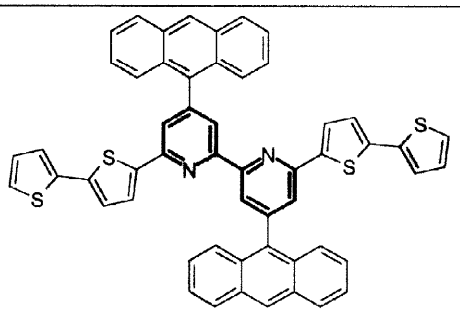
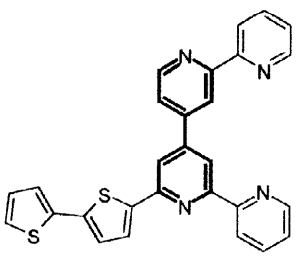
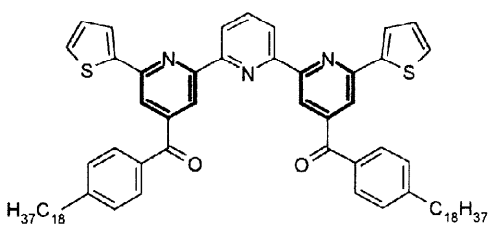
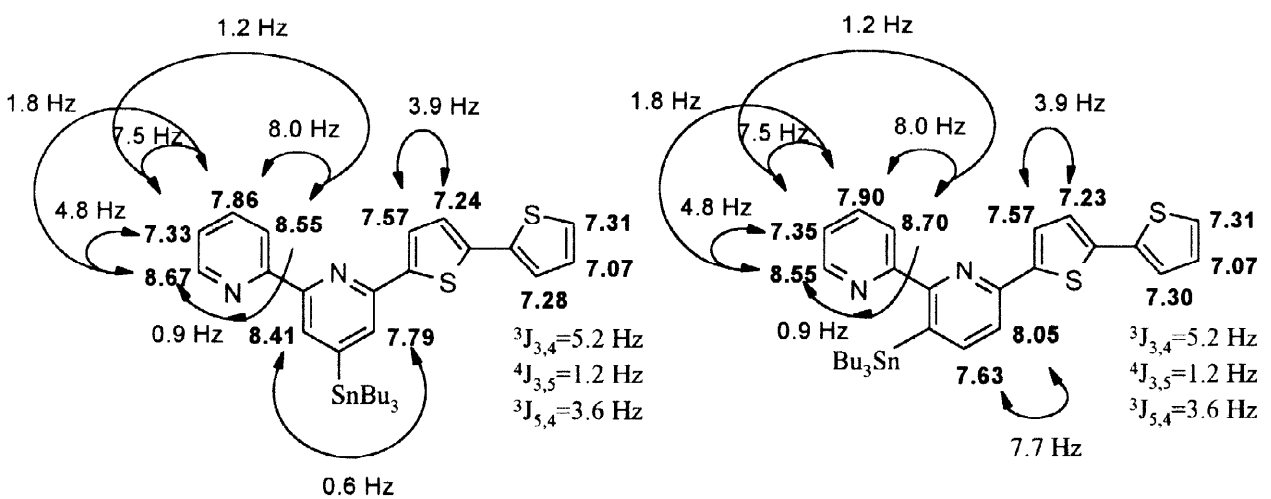
Tin compound	R^1-X	4-Tributylstannyl-pyridine		Reaction times [h]	Yield [%]	M.P. [°C]
4a	**5c**	**6a**		20	74	295-299
4b	**5a**	**6b**		24	58	286-288
4c	**5a**	**6c**		48	51	319-323
4d	**5a**	**6d**		42	42	274-276
4e	**5b**	**6e**		48	54	130-131
4f	**5b**	**6f**		16	72	188-190

Table 5b. Synthesis of 4-aryl-pyridines **4** according to Scheme 4.

Tin compound	R^1-X	4-Tributylstannyl-pyridine	Reaction conditions	Yield [%]	M.P. [°C]
4c	**5d**	**6g** 	5d	74	209-211
4a	**5e**	**6h** 	48h	41	261-265
4d	**5f**	**6i** 	50h	82	141-144

^{1}H NMR spectra: All structures of new compounds were confirmed by the expected chemical shifts and coupling constants. As an example, Scheme 5 shows the ^{1}H NMR data for **4a** and its 3-isomer.



4a

Scheme 5. ^{1}H NMR data (CD_2Cl_2, 250 MHz) of **4a** (left) and of its 3-isomer (right).

The δ and *J* values for the butyl group and Sn-H couplings are not shown. While the coupling constants of the "inner" pyridine ring are significantly different for the two isomers, the other coupling constants do not change at all. The "meta"-coupling (^4J=0.6 Hz) of the "inner" pyridine ring can be assigned unequivocally to the 4-isomer **4a** whereas the "ortho"-coupling (^3J=7.7 Hz) is assigned to the 3-isomer. Further evidence for this regiochemistry results from the ^{119}Sn-^{1}H couplings with coupling constants $^3J\approx$37 Hz for **4a**. Conversions of 4-tributylstannyl-pyridines **4** to coupling products **6** are in line with the assigned regiochemistry.

UV/VIS and fluorescence spectra: 1,2,4-Triazines **3** and oligopyridines **6** show intense yellow to green fluorescences (Table 6) if one or more oligothienyl substituents are present in the molecule. Figure 1 shows the absorption- and emission-spectrum of 1,2,4-triazine **3a** in dichloromethane at 20°C.

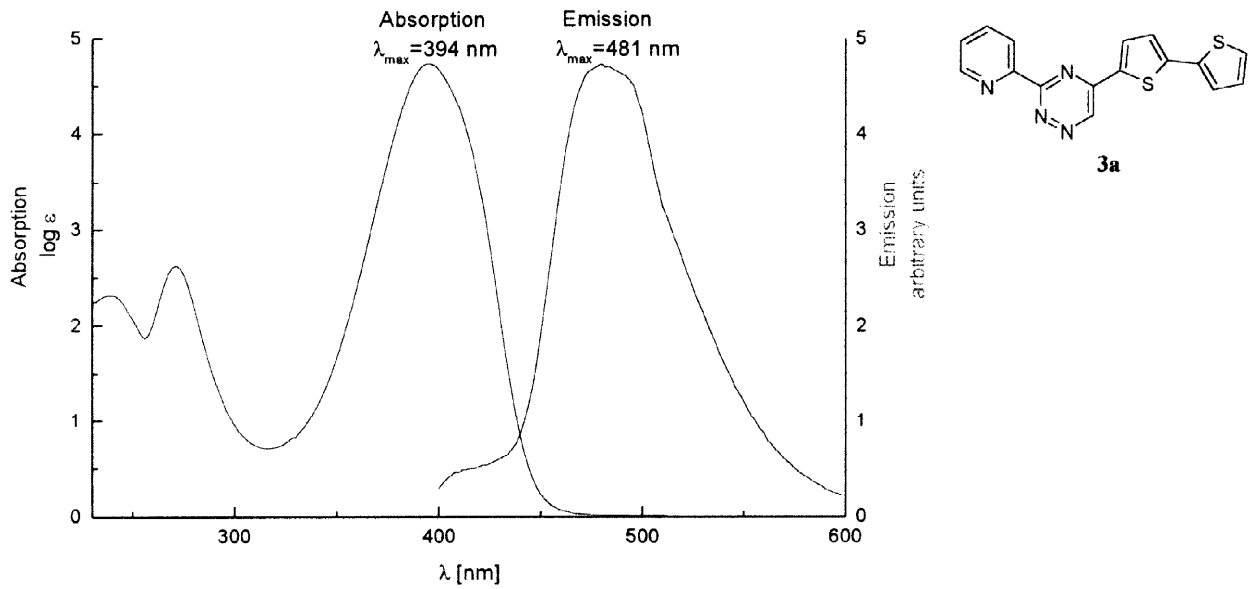


Figure 1. Absorption- and emission-spectrum of **3a** in dichloromethane, 20°C

The Stokes shift of **3a** (87 nm) is relatively low compared to the other compounds listed in Table 6. The Stokes shift of compound **6e** (114 nm) is the highest one in this series.

The excitation wavelength shown in Table 6 is equal to the absorption maximum in the UV/VIS spectra. Due to the oligothienyl substituents, π-π^* transitions are shifted bathochromically and cause the yellow colour of oligopyridines **6a**, **6c**, **6e**, **6g**, **6h**. If no oligothiophene moiety is present as in compounds **6b**, **6d**, **6f** and **6i**, these compounds are colourless and nonflourescent.

Table 6. Excitation and emission wavelengths of 1,2,4-triazines **3** and oligopyridines **6** in dichloromethane.

Compound	**3a**	**3c**	**3e**	**6a**	**6c**	**6e**
Excitation [nm]	394	410	394	394	370	328
Emission [nm]	481	494	498	480	446	442
Stokes shift [nm]	87	84	104	86	76	114

Protonation of oligopyridines **6** leads to a bathochromic shift of the emission wavelength. If to a solution of **6e** in methanol, for instance, trifluoroacetic acid is added, the emission wavelength is shifted from 445 nm (unprotonated) to 502 nm (protonated). Addition of an equimolar amount of base shifts the emission wavelength back to the initial value. Thus, compound **6e** may serve as a fluorescence related pH indicator.

CONCLUSION

Our 'LEGO' System offers a new and simple approach to thienyl-substituted 4-stannylated 2,6-oligopyridines and their coupling products regioselectively. The 4-stannylated compounds **4** are easily obtained by [4+2] cycloaddition reactions of 1,2,4-triazines **3** with ethynyltibutyltin in 1,2-dichlorobenzene. Replacement of the tributyltin group leads to novel 4-substituted 2,6-oligopyridines **6**. These thienyl-substituted oligopyridines show interesting pH sensitive fluorescence properties. Further work using these 2,6-oligopyridines **6** and stannylated 2,6-oligopyridines **4** as polydentate ligands in Ru^{II} complexes is in progress. Recent investigations [22, 23] showed that all reactions performed with the ligands can also be done with their Ru^{II} complexes.

EXPERIMENTAL SECTION

General: IR spectra were recorded with a Beckmann Acculab I. NMR spectra were obtained with a Bruker AC250 and ARX400 (250 MHz / 400 MHz for ^{1}H and 63 MHz / 100 MHz for ^{13}C). The degree of substitution of the C atoms was determined by the DEPT-135 method. Mass spectra were recorded either with an ionizing voltage of 70 eV by electron impact with a Varian CH90 instrument or by field desorption with a Varian 311A instrument. UV/Vis spectra were recorded with a Karl Zeiss Specord M500. Fluorescence spectra were recorded with an Aminco-Bowman Series 2 luminescence spectrometer. Melting points were determined with a Büchi melting point apparatus and are uncorrected. Elemental analyses were performed in the Microanalytical Laboratory of the University of Regensburg. For analytical thin layer chromatography precoated plastic sheets (POLYGRAM SIL G/UV254, Macherey-Nagel) were used. Silica gel 60 (particle size 0.040 - 0.063 mm, Merck) was used for flash column

chromatography (fcc). Cycloaddition and coupling reactions were carried out under an atmosphere of nitrogen in solvents dried according to standard procedures.
2-Bromo-thiophene **5a** and 9-bromo-anthracene **5d** were purchased from Aldrich and used without further purification. 6,6'-Dicyano-[2,2']-bipyridine [24], ethynyltributyltin [25], tetrakis-(triphenylphosphine)palladium(0) [26] and benzylchlorobis(triphenyl-phosphine)palladium(II) [27] were prepared according to literature procedures. p-Octadecyl-benzoyl chloride was prepared from p-octadecyl-benzoic acid [28] by treatment with thionyl chloride.

[2,2']-Bipyridine-6,6'-dicarboxbisamidrazone (**1d**): 3.50 g (17.0 mmol) of 6,6'-dicyano-[2,2']-bipyridine, suspended in 150 ml of reagent grade ethanol, was treated with 16.5 ml (17.0 g, 340 mmol) of hydrazine hydrate (100%). After stirring at ambient temperature for 17 d the precipitate was isolated by suction filtration, washed with 50 ml of ethanol and dried at 30°C/0.01 Torr, yielding 4.37 g (16.2 mmol, 95%) of **1d**, colourless crystals, m.p. >450°C (decomp. at 440°C). **1d** was used without any further purification. - IR (KBr): ν = 3440, 3290, 3190, 3000, 1645, 1610, 1555, 1435, 1060, 875, 800, 795 cm^{-1}. - ^1H NMR (DMSO-d_6, 250 MHz): δ = 5.50 (s, 4 H), 5.98 (s, 4 H), 7.89 (dd, 2 H, J=8.0 Hz, J=7.5 Hz), 7.97 (dd, 2 H, J=8.0 Hz, J=1.3 Hz), 8.61 (dd, 2 H, J=7.5 Hz, J=1.3 Hz) ppm. **1d** was identified by the successful preparation of **3f**.

5,5'-Bis-[2,2']-bithiophen-5-yl-[3,3']bi[1,2,4]-triazine (**3c**): Dicarboxbisamidrazone **1b** (387 mg, 3.33 mmol) and 5-[2,2']-bithiophene-glyoxal hydrate **2b** [19] (1.60 g, 6.66 mmol) were dissolved in 50 ml ethanol (99%) and stirred 2 d at ambient temperature. The crude product obtained after heating to reflux for 3 h and cooling to 0°C was separated by suction filtration. Recrystallization from *N,N*-dimethylformamide yielded **3c** (1.41 g, 3.32 mmol, 97%) as orange solid, m.p. 238-240°C. - IR (KBr): ν = 3070, 1550, 1530, 1450, 1320, 1160, 1100, 1020, 960, 850, 810 cm^{-1}. - ^1H NMR (250 MHz, DMF-d_7): δ = 7.23 (dd, 2 H, J=5.1 Hz, J=3.7 Hz), 7.66 (d, 2 H, J=4.1 Hz), 7.68 (dd, 2 H, J=3.7 Hz, J=1.1 Hz), 7.75 (dd, 2 H, J=5.1 Hz, J=1.1 Hz), 8.55 (d, 2 H, J=4.1 Hz), 10.26 (s, 2 H) ppm. - EI MS (70eV); m/z (%): 488 (15) [M^+], 460 (4) [$M^+ - N_2$], 270 (6) [$M^+ - C_{10}H_6N_2S_2$], 244 (2) [M^{2+}], 190 (100) [$M^+ - C_{12}H_5N_6S_2$]. -UV/Vis (CH_2Cl_2): 274 nm (8250 $l \cdot mol^{-1}cm^{-1}$, lg ε 3.917), 410 nm (27168 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.434). - $C_{22}H_{12}N_6S_4$ (488.6): calcd. C 54.08, H 2.48, N 17.20; found C 53.95, H 2.82, N 17.07.

2,6-Bis-[5-[2,2']-bithiophen-5-yl][1,2,4]-triazine-3-yl]-pyridine (**3e**): Pyridine-2,6-di-carboxamidrazone **1c** (606 mg, 3.12 mmol) and 5-[2,2']-bithiophene-glyoxal hydrate **2b** (1.50 g, 6.24 mmol) were dissolved in 35 ml ethanol (99%) and the resulting yellow solution was stirred 1 d at ambient temperature, followed by heating to reflux for 3 h. The solvent was stripped off and the solid residue was recrystallized from *N,N*-dimethylformamide to yield **3e** (1.42 g, 2.51

mmol, 81%) as bright yellow crystals, m.p. 283-285°C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3110, 3080, 1550, 1530, 1490, 1450, 1400, 1330, 1260, 1230, 1150, 1120, 1090, 1060, 1020, 990, 870, 850, 780, 730 cm^{-1}. - ^1H NMR (400 MHz, DMSO-d_6): δ = 7.08 (dd, 2 H, J=5.1 Hz, J=3.7 Hz), 7.53 (dd, 2 H, J=3.6 Hz, J=1.2 Hz), 7.61 (dd, 2 H, J=5.1 Hz, J=1.2 Hz), 7.62 (d, 2 H, J=3.9 Hz), 8.37 (t, 1 H, J=7.8 Hz), 8.44 (d, 2 H, J=4.1 Hz), 8.68 (d, 2 H, J=7.8 Hz), 10.09 (s, 2 H) ppm. - EI MS (70eV); m/z (%): 565 (6) [M^+], 509 (1) [M^+ - 2 N_2], 347 (45) [M^+ - $C_{10}H_6N_2S_2$], 222 (8) [M^+ - $C_{17}H_5N_5S_2$], 190 (100) [M^+ - $C_{17}H_9N_7S_2$]. - UV/Vis (CH_2Cl_2): 272 nm (22784 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.358), 394 nm (55010 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.740). - $C_{27}H_{15}N_7S_4$ (565.7): calcd. C 57.33, H 2.67, N 17.33; found C 56.77, H 3.22, N 16.83.

General procedure for the synthesis of 1,2,4-triazines **3b**, **3d** *and* **3f**: A mixture of amidrazone and 2-thienylglyoxal (1 eq.) in ethanol (99%) was heated under reflux for 6 h. After cooling the yellow precipitate was separated by suction filtration, washed with cold ethanol, recrystallized and dried at 60°C/0.01 Torr.

5,5'-Di-thiophen-2-yl-3,3'-bi-[1,2,4]-triazine (**3b**): Following the *general procedure* **1b** (500 mg, 4.31 mmol) and **2a** [18] (1.21 g, 8.61 mmol) yielded after recrystallization from dichloromethane 1.11 g (3.42 mmol, 79%) of **3b**, yellow crystals, m.p. 245-247°C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3060, 3010, 1530, 1500, 1470, 1410, 1135, 1000, 715 cm^{-1}. - ^1H NMR (CD_2Cl_2, 250 MHz): δ = 7.32 (dd, 2 H, J=5.0 Hz, J=3.9 Hz), 7.81 (dd, 2 H, J=5.0 Hz, J=1.1 Hz), 8.11 (dd, 2 H, J=3.9 Hz, J=1.1 Hz), 9.69 (s, 2 H) ppm. - EI MS (70 eV); m/z (%): 324 (18) [M^+], 296 (4) [M^+ - N_2], 188 (1) [M^+ - N_2 - C_6H_4S], 108 (100) [$C_6H_4S^+$], 82 (3) [$C_4H_2S^+$]. - $C_{14}H_8N_6S_2$ (324.4): calcd. C 51.83, H 2.49, N 25.91; found C 51.70, H 2.77, N 26.07.

2,6-Bis(5-thiophen-2-yl-3,3'-[1,2,4]-triazin-3-yl)-pyridine (**3d**): Following the *general procedure* **1c** (5.80 g, 30.0 mmol) and **2a** (8.41 g, 60.0 mmol) yielded after recrystallization from *N,N*-dimethylformamide 10.5 g (26.1 mmol, 87%) of **3d**, yellow needles, m.p. 261-263°C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3060, 3010, 1530, 1500, 1475, 1410, 1400, 1375, 1320, 1110, 980, 705 cm^{-1}. - ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.30 (dd, 2 H, J=5.0 Hz, J=3.8 Hz), 7.76 (dd, 2 H, J=5.0 Hz, J=1.1 Hz), 8.11 (dd, 2 H, J=3.8 Hz, J=1.1 Hz), 8.20 (t, 1 H, J=7.9 Hz), 8.82 (d, 2 H, J=7.9 Hz), 9.58 (s, 2H) ppm. - EI MS (70 eV); m/z (%): 401 (13) [M^+], 373 (1) [M^+ - N_2], 265 (3) [M^+ - N_2 - C_6H_4S], 108 (100) [$C_6H_4S^+$], 82 (2) [$C_4H_2S^+$]. - $C_{19}H_{11}N_7S_2$ (401.5): calcd. C 56.84, H 2.76, N 24.43; found C 56.71, H 3.03, N 24.50.

6,6'-Bis(5-thiophen-2-yl-3,3'-[1,2,4]-triazin-3-yl)-[2,2']-bipyridine (**3f**): Following the *general procedure* **1d** (2.00 g, 7.40 mmol) and **2a** (2.07 g, 14.8 mmol) yielded after recrystallization from *N,N*-dimethylformamide 2.97 g (6.21 mmol, 84%) of **3f**, golden plates,

m.p. 303-306°C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3080, 3060, 1575, 1535, 1505, 1485, 1390, 1350, 1320, 1260, 1110, 705 cm^{-1}. - ^1H NMR (DMF-d_7, 400 MHz): δ = 7.38 (dd, 2 H, J=5.0 Hz, J=3.8 Hz), 8.04 (dd, 2 H, J=5.0 Hz, J=1.1 Hz), 8.28 (dd, 2 H, J=7.8 Hz, J=7.8 Hz), 8.40 (dd, 2 H, J=3.8 Hz, J=1.1 Hz), 8.59 (d, 2 H, J=7.8 Hz), 8.91 (d, 2 H, J=7.9 Hz), 9.93 (s, 2H) ppm. - EI MS (70 eV); m/z (%): 478 (1) [M^+], 449 (2) [M^+ + 2H - N_2], 423 (1) [M^+ + 2H - 2N_2], 342 (2) [M^+ - N_2 - C_6H_4S],], 314 (8) [M^+ - 2N_2 - C_6H_4S],], 206 (1) [M^+ - 2N_2 - 2C_6H_4S], 108 (100) [$C_6H_4S^+$], 82 (3) [$C_4H_2S^+$]. - $C_{24}H_{14}N_8S_2$ (401.5): calcd. C 60.23, H 2.95, N 23.42; found C 59.93, H 3.21, N 23.18.

General procedure for the synthesis of tributyltin-pyridines **4a-f**: The appropriate 1,2,4-triazine **3** and a 1.2 fold molar excess (per triazine ring) of ethynyltributyltin were heated in 1,2-dichlorobenzene under an atmosphere of nitrogen. For reaction times and temperatures see Table 3. The solvent was stripped off and the residue was purified by fcc on silica gel.

6-[2,2']-Bithiophen-5-yl-4-tributylstannyl-[2,2']-bipyridine (**4a**): Following the *general procedure* **3a** (1.50 g, 4.65 mmol) and ethynyltributyltin (1.77 g, 5.60 mmol) yielded after fcc (petroleum ether 40/60 : ethyl acetate 98 : 2) 1.87 g (3.07 mmol, 66%) of **4a**, slight yellow oil. - IR (film): $\tilde{\nu}$ = 3060, 2950, 2920, 2870, 2840, 1580, 1560, 1550, 1520, 1470, 1460, 1380, 1320, 1240, 1120, 1040, 1000, 860, 840, 790, 740, 690 cm^{-1}. - ^1H NMR (CD_2Cl_2, 250 MHz): δ= 0.91 (t, 9H, J=7.2 Hz), 1.26-1.17 (m, 6H), 1.45-1.30 (m, 6H), 7.07 (dd, 1H, J=5.1 Hz, J=3.6 Hz), 7.24 (d, 1H, J=3.9 Hz), 7.28 (dd, 1H, J=5.2 Hz, J=1.2 Hz), 7.31 (dd, 1H, J=3.5 Hz, J=1.2 Hz), 7.33 (ddd, J=7.5 Hz, J=4.8 Hz, J=1.3 Hz), 7.57 (d, 1H, J=3.9 Hz), 7.79 (d, 1H, J=0.6 Hz), 7.86 (ddd, 1H, J=8.0 Hz, J=7.5 HZ, J=1.9 Hz), 8.41 (d, 1H, J=0.6 Hz), 8.55 (ddd, 1H, J=8.0 Hz, J=1.2 Hz, J=0.9 Hz), 8.67 (ddd, 1H, J=4.8 Hz, J=1.8 Hz, J=0.9 Hz) ppm. - ^{13}C NMR (CD_2Cl_2, 63 MHz, DEPT): δ= 10.14 (3 C, -), 13.84 (3 C, +), 27.75 (3 C, -), 29.45 (3 C, -), 121.61 (1 C, +), 123.98 (1 C, +), 124.32 (1 C, +), 124.90 (1 C, +), 125.08 (1 C, +), 125.21 (1 C, +), 126.65 (1 C, +), 127.45 (1 C, +), 128.36 (1 C, +), 137.11 (1 C, +), 138.06 (1 C, 0), 139.46 (1 C, 0), 145.07 (1 C, 0), 149.45 (1 C, +), 150.14 (1 C, 0), 153.93 (1 C, 0), 155.40 (1 C, 0), 156.78 (1 C, 0), ppm. - FD MS (CH_2Cl_2); *m/z* (%): 1218 (< 20) [M_2^+], 1161 (< 5) [M_2^+ - C_4H_9], 610 (100) [M^+], 565 (< 5) [M^+ - C_4H_9]. - $C_{30}H_{38}N_2S_2Sn$ (609.5): calcd. C 59.12, H 6.28, N 4.60; found C 59.27, H 6.49, N 4.50.

6,6''-Di-thiophen-2-yl-4,4'-bis-tributylstannyl-[2,2']-bipyridine (**4b**): Following the *general procedure* **3b** (500 mg, 1.54 mmol) and ethynyltributyltin (1.94 g, 6.17 mmol) yielded after fcc (petroleum ether 40/60 : ethyl acetate 98 : 2) 1.02 g (1.14 mmol, 74%) of **4b**, colourless oil. - IR (film): $\tilde{\nu}$ = 3090, 3050, 3005, 2930, 2900, 2850, 2830, 1540, 1520, 1505, 1445, 1440, 1420,

1345, 1115, 845, 725, 680 cm^{-1}. - ^1H NMR (CD_2Cl_2, 250 MHz): δ = 0.92 (t, 18 H, J=7.3 Hz), 1.20 - 1.30 (m, 12 H), 1.35 - 1.55 (m, 12H), 1.60 - 1.75 (m, 12 H), 7.15 (dd, 2 H, J=5.1 Hz, J=3.7 Hz), 7.43 (dd, 2 H, J=5.1 Hz, J=1.1 Hz), 7.68 (dd, 2 H, J=3.7 Hz, J=1.1 Hz), 7.80 (d, 2 H, J=0.6 Hz), 8.43 (d, 2 H, J=0.6 Hz) ppm. - ^{13}C NMR (CD_2Cl_2, 63 MHz, DEPT): δ = 10.24 (6C, -), 13.84 (6 C, +), 27.79 (6 C, -), 29.49 (6 C, -), 124.44 (2 C, +), 126.76 (2 C, +), 127.62 (2 C, +), 127.83 (2 C, +), 128.32 (2 C, +), 146.55 (2 C, 0), 150.35 (2 C, 0), 153.95 (2 C, 0), 155.27 (2 C, 0).- FD MS (toluene); m/z (%): 954 (<5) [$M^+ + C_4H_8$], 898 (100) [M^+], 841 (<5) [$M^+ - C_4H_9$]. - $C_{42}H_{64}N_2S_2Sn_2$ (898.5): calcd. C 56.14, H 7.18, N 3.12; found C 56.13, H 7.19, N 3.13.

6,6′-Bis-[2,2′]-bithiophen-5-yl-4,4′-bis-tributylstannyl-[2,2′]-bipyridine (**4c**): Following the *general procedure* **3c** (650 mg, 1.33 mmol) and ethynyltributyltin (1.05 g, 3.33 mmol) yielded after fcc (petroleum ether 40/60, subsequently petroleum ether : ethyl acetate 4:1) 900 mg (0.85 mmol, 64%) of **4c**, yellowish solid, m.p. 51-52°C. - IR (film): $\tilde{\nu}$ = 3080, 2970, 2940, 2880, 2860, 1560, 1520, 1460, 1420, 1360, 1270, 1200, 1130, 1080, 1000, 860, 840, 780, 700 cm^{-1}. - ^1H NMR (CD_2Cl_2, 250 MHz): δ= 0.93 (t, 18 H, J=7.3 Hz), 1.28-1.21 (m, 12 H), 1.50-1.30 (m, 12 H), 1.75-1.61 (m, 12 H), 7.07 (dd, 2 H, J=5.2 Hz, J=3.6 Hz), 7.24 (d, 2 H, J=3.9 Hz), 7.28 (dd, 2 H, J= 5.1 Hz, J= 1.2 Hz), 7.30 (dd, 2 H, J=5.5 Hz, J=1.2 Hz), 7.58 (d, 2 H, J=3.9 Hz), 7.8 (d, 2 H, J=0.5 Hz), 8.58 (d, 2H, J=0.4 Hz) ppm. - ^{13}C NMR (CD_2Cl_2, 63 MHz, DEPT): δ= 10.21 (6 C, -), 13.94 (6 C, +), 27.87 (6 C, -), 29.51 (6 C, -), 124.29 (2 C, +), 124.94 (2 C, +), 125.12 (2 C, +), 125.14 (2 C, 0), 126.57(2 C, +), 127.87 (2 C, +), 128.34 (2 C, +), 138.08 (2 C, 0), 139.42 (2 C, 0), 145.23 (2 C, 0), 150.03 (2 C, 0), 153.81 (2 C, 0), 155.32 (2 C, 0) ppm. - FD MS (CH_2Cl_2); *m/z* (%): 1063 (100) [M^+], 1007 (< 5) [$M^+ - C_4H_9$], 532 (< 15) [M^{2+}]. - $C_{50}H_{68}N_2S_4Sn_2$ (1063.0): calcd. C 56.51, H 6.45, N 2.64; found 56.38, 6.51, 2.35.

6,6′′-Di-thiophen-2-yl-4,4′-bis-tributylstannyl-[2,2′,6′,2′′]-terpyridine (**4d**): Following the *general procedure* **3d** (2.50 g, 6.23 mmol) and ethynyltributyltin (7.85 g, 24.9 mmol) yielded after fcc (petroleum ether 40/60 : ethyl acetate 98 : 2) 3.51 g (3.60 mmol, 58%) of **4d**, colourless oil. - IR (film): $\tilde{\nu}$ = 3070, 3030, 2960, 2930, 2870, 2850, 1560, 1530, 1520, 1460, 1450, 1435, 1410, 1370, 1120, 820, 695 cm^{-1}. - ^1H NMR (CD_2Cl_2, 250 MHz): δ = 0.91 (t, 18 H, J=7.3 Hz), 1.22 - 1.30 (m, 12 H), 1.31 - 1.47 (m, 12H), 1.58 - 1.72 (m, 12 H), 7.17 (dd, 2 H, J=5.1 Hz, J=3.7 Hz), 7.44 (dd, 2 H, J=5.1 Hz, J=1.1 Hz), 7.70 (dd, 2 H, J=3.7 Hz, J=1.1 Hz), 7.84 (d, 2 H, J=0.6 Hz), 8.01 (t, 1 H, J=7.9 Hz), 8.59 (d, 2 H, J=0.6 Hz), 8.61 (d, 2 H, J=7.9 Hz) ppm. - ^{13}C NMR (CD_2Cl_2, 63 MHz, DEPT): δ = 10.24 (6C, -), 13.86 (6 C, +), 27.72 (6 C, -), 29.50 (6 C, -), 121.71 (2 C, +), 124.65 (2 C, +), 127.03 (2 C, +), 127.29 (2 C, +), 127.80 (2 C, +), 128.41 (2 C, +), 138.10 (1 C, +), 146.34 (2 C, 0), 150.49 (2 C, 0), 154.02 (2 C, 0), 155.29 (2 C, 0), 156.16 (2 C, 0). - FD MS (toluene); m/z (%): 1208 (<30) [$M^+ + H + Sn(C_4H_9)_2$], 1033 (<10) [$M^+ + H +$

C_4H_9], 975 (100) [M^+], 917 (<5) [M^+ - H - C_4H_9]. - $C_{47}H_{67}N_3S_2Sn_2$ (975.6): calcd. C 57.87, H 6.92, N 4.31; found C 57.83, H 6.89, N 4.22.

6,6''-Bis-[2,2']-bithiophen-5-yl-4,4''-bis-tributylstannyl-[2,2';6',2'']-terpyridine (**4e**): Following the *general procedure* **3e** (1.00 g, 1.77 mmol) and ethynyltributyltin (1.45 g, 4.60 mmol) yielded after fcc (petroleum ether 40/60, subsequently petroleum ether : ethyl acetate 98 : 2) 860 mg (0.75 mmol, 43%) of **4e**, yellowish solid, m.p. 40-41°C. - IR (film): $\tilde{\nu}$ = 3070, 2960, 2920, 2880, 2860, 1560, 1520, 1460, 1450, 1370, 1240, 1120, 1070, 870, 840, 820, 790, 760, 690 cm^{-1}. - ^1H NMR (CD_2Cl_2, 250 MHz): δ = 0.91 (t, 18 H, J=7.3 Hz), 1.31-1.23 (m, 12 H), 1.46-1.34 (m, 12 H), 1.71-1.59 (m, 12 H), 7.09 (dd, 2 H, J=5.2 Hz, J=3.6 Hz), 7.26 (d, 2 H, J=3.8 Hz), 7.30 (dd, 2 H, J=5.2 Hz, J=1.2 Hz), 7.34 (dd, 2 H, J=3.6 Hz, J=1.2 Hz), 7.60 (d, 2 H, J=3.8 Hz), 7.83 (d, 2 H, J=0.6 Hz), 8.05 (dd, 1 H, J=8.0 Hz, J=7.7 Hz), 8.59 (d, 2 H, J=0.6 Hz), 8.63 (d, 2 H, J=7.8 Hz) ppm. - ^{13}C NMR (CD_2Cl_2, 63 MHz, DEPT): δ = 10.15 (6 C, -), 13.89 (6 C, +), 27.73 (6 C, -), 29.46 (6 C, -), 121.73 (2 C, +), 124.31 (2 C, +), 124.87 (2 C, +), 125.09 (2 C, +), 125.21 (2 C, +), 126.65 (2 C, +), 127.25 (2 C, +), 128.39 (2 C, +), 137.99 (2 C, 0), 138.12 (1 C, +), 139.44 (2 C, 0), 144.96 (2 C, 0), 150.05 (2 C, 0), 153.85 (2 C, 0), 155.26 (2 C, 0), 155.94 (2 C, 0). - FD MS (CH_2Cl_2); *m/z* (%) 1196 (< 5) [M^+ + C_4H_9], 1139 (100) [M^+], 1082 (< 5) [M^+ - C_4H_9], 906 (< 5) [M^+ -$C_{12}H_{27}Sn$ + C_4H_9], 851 (< 5), [M^+ - $C_{12}H_{27}Sn$]. - $C_{55}H_{71}N_3S_4Sn$ (1139.9): calcd. C 57.95, H 6.28, N 3.69; found C 57.90, H 6.16, N 3.70.

6,6'''-Di-thiophen-2-yl-4,4'''-bis-tributylstannyl-[2,2',6',2'',6'',2''']-quaterpyridine (**4f**): Following the *general procedure* **3f** (2.00 g, 4.18 mmol) and ethynyltributyltin (7.87 g, 25.0 mmol) yielded after fcc (petroleum ether 40/60 : ethyl acetate 98 : 2) 1.47 g (1.40 mmol, 34%) of **4f**, colourless crystals, m.p. 115-117°C. - IR (KBr): $\tilde{\nu}$ = 3050, 2930, 2890, 2820, 1545, 1510, 1445, 1425, 1405, 1365, 1235, 1110, 1100, 1060, 845, 795, 695, 650 cm^{-1}. - ^1H NMR (CD_2Cl_2, 250 MHz): δ = 0.95 (t, 18 H, J=7.3 Hz), 1.21 - 1.30 (m, 12 H), 1.34 - 1.53 (m, 12H), 1.60 - 1.76 (m, 12 H), 7.17 (dd, 2 H, J=5.1 Hz, J=3.7 Hz), 7.45 (dd, 2 H, J=5.1 Hz, J=1.1 Hz), 7.70 (dd, 2 H, J=3.7 Hz, J=1.1 Hz), 7.85 (d, 2 H, J=0.6 Hz), 8.04 (dd, 2 H, J=7.8 Hz, J=7.8 Hz), 8.63 (dd, 2 H, J=7.8 Hz, J=1.1 Hz), 8.70 (dd, 2 H, J=7.8 Hz, J=1.1 Hz), 8.71 (d, 2 H, J=0.6 Hz) ppm. - ^{13}C NMR (CD_2Cl_2, 63 MHz, DEPT): δ = 10.28 (6C, -), 13.85 (6 C, +), 27.80 (6 C, -), 29.53 (6 C, -), 121.11 (2 C, +), 121.67 (2 C, +), 124.66 (2 C, +), 127.12 (2 C, +), 127.64 (2 C, +), 127.73 (2 C, +), 128.38 (2 C, +), 138.11 (1 C, +), 146.35 (2 C, 0), 150.56 (2 C, 0), 153.87 (2 C, 0), 155.38 (2 C, 0), 155.79 (2 C, 0), 156.12 (2 C, 0). - FD MS (CH_2Cl_2); m/z (%): 1285 (<5) [M^+ + H + $Sn(C_4H_9)_2$], 1111 (<5) [M^+ + H + C_4H_9], 1053 (<10) [M^+ + H], 995 (100) [M^+ - C_4H_9], 531 (<65) [M^+ - $Sn_2(C_4H_9)_5$], 526 (<5) [M^{2+}]. - $C_{52}H_{70}N_4S_2Sn_2$ (1052.7): calcd. C 59.33, H 6.70, N 5.32; found C 59.40, H 6.82., N 5.09.

General procedure for the synthesis of coupling products ***6a-h***: $Pd(PPh_3)_4$ (app. 10 mg, 2 mol%) was dissolved in 4 ml toluene. The aryl bromide (0.75 mmol, 1.2 fold molar excess) was added and the reaction mixture stirred for 5 min. After this period the tributyltin compound **4** (60 mmol) in 2 ml toluene was added and the reaction mixture heated to reflux for the time indicated in Tables 5a, 5b. In most cases the precipitation of palladium indicated the end of the reaction. After filtration and stripping off the solvent the residue was purified by recrystallization or fcc.

6-[2,2']-bithiophen-5-yl-4-[2,2';5',2'']-terthiophen-5-yl-[2,2']-bipyridinyl (**6a**): Following the *general procedure* 5-bromo-[2,2';5',2'']-terthiophene **5c** (322 mg, 0.98 mmol) and **4a** (400 mg, 0.66 mmol) yielded after filtration on a short silica gel column with CH_2Cl_2 as eluent 276 mg (0.49 mmol, 74%) of **6a**, yellow solid, m.p. 295-299°C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3120, 3070, 1600, 1580, 1550, 1460, 1420, 1400, 1250, 1220, 1110, 1070, 1050, 840, 790, 740, 700 cm^{-1}. - ^1H NMR (DMSO-d_6, 400 MHz): δ = 7.14 (dd, 1 H, J=5.1 Hz, J=3.6 Hz), 7.16 (dd, 1 H, J=5.1 Hz, J=3.6 Hz), 7.36 (d, 1 H, J=3.6 Hz), 7.41 (dd, 1 H, J=3.5 Hz, J=1.2 Hz), 7.46 (d, 1 H, J=3.7 Hz), 7.49 (d, 1 H, J=3.7 Hz), 7.49 (dd, 1 H, J=3.6 Hz, J=1.2 Hz), 7.54 (d, 1 H, J=3.7 Hz), 7.55 (ddd, 1 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.58 (dd, 1 H, J=5.1 Hz, J=1.2 Hz), 7.59 (dd, 1 H, J=5.1 Hz, J=1.2 Hz), 8.07 (ddd, 1 H, J=8.0 Hz, J=7.5 Hz, J=1.8 Hz), 8.08 (d, 1 H, J=3.2 Hz), 8.09 (d, 1 H, J=3.2 Hz), 8.36 (d, 1 H, J=1.6 Hz), 8.43 (d, 1 H, J=1.6 Hz), 8.50 (ddd, 1 H, J=8.0Hz, J=1.2 Hz, J=0.9Hz), 8.78 (ddd, 1 H, J=4.8 Hz, J=1.8 Hz, J=0.9 Hz) ppm. - EI MS (70eV); *m/z* (%): 566 (100) [M^+], 534 (10) [M^+ - SH], 248 (13) [M^+ - $C_{18}H_{11}N_2S_2$], 167 (4) [M^+ - $C_{22}H_{13}N_2S_3$], 78 (5) [M^+ - $C_{25}H_{14}NS_5$]. UV/Vis (CH_2Cl_2): 394 nm (61974 $l \cdot mol^{-1}cm^{-1}$, lg ε 4.792). - $C_{30}H_{18}N_2S_5$ (566.8): calcd. C 63.57, H 3.20, N 4.94; found C 63.60, H 3.19, N 4.89.

4,4',6,6'-Tetra-thiophen-2-yl-[2,2']-bipyridine (**6b**): Following the *general procedure* **4b** (516 mg, 574 µmol) and 2-bromo-thiophene **5a** (219 µl, 375 mg, 2.30 mmol) yielded after recrystallization from acetonitrile 162 mg (335 µmol, 58%) of **6b**, slight yellow needles, m.p. 286-288°C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3070, 3040, 1570, 1535, 1500, 1415, 1370, 1225, 860, 840, 815, 740, 680 cm^{-1}. - ^1H NMR (CD_2Cl_2, 250 MHz): δ = 7.21 (dd, 2 H, J=5.1 Hz, J=3.7 Hz), 7.24 (dd, 2 H, J=5.1 Hz, J=3.7 Hz), 7.50 (dd, 2 H, J=5.1 Hz, J=1.2 Hz), 7.53 (dd, 2 H, J=5.1 Hz, J=1.2 Hz), 7.76 (dd, 2 H, J=3.7 Hz, J=1.2 Hz), 7.79 (dd, 2 H, J=3.7 Hz, J=1.2 Hz), 7.93 (d, 2 H, J=1.6 Hz), 8.70 (d, 2 H, J=1.6 Hz) ppm. - FD MS (toluene); m/z (%): 484.2 (100) [M^+], 242.1 (<10) [M^{2+}]. - $C_{26}H_{16}N_2S_4$ (484.69): calcd. C 64.42, H 3.33, N 5.78; found C 64.31, H 3.61, N 5.70.

6,6′-Di-[2,2′]-bithiophen-5-yl-4,4′-di-thiophen-2-yl-[2,2′]-bipyridine (**6c**): Following the *general procedure* 2-bromo-thiophene **5a** (31 mg, 0.19 mmol) and **4c** (160 mg, 0.15 mmol) yielded after recrystallization from DMSO 50.0 mg (0.77 mmol, 51%) of **6c**, colourless solid, m.p. 319-323°C (decomp.). No deposition of palladium was observed in this case. - IR (KBr): $\tilde{\nu}$ = 3100, 3060, 1580, 1570, 1540, 1460, 1430, 1390, 1250, 1240, 1200, 1080, 990, 870, 850,840, 800, 760, 690 cm^{-1}. - ^1H NMR (DMSO-d_6, 400MHz, 120°C): δ = 7.13 (dd, 2 H, J=5.1 Hz, J=3.6 Hz), 7.29 (dd, 2 H, J=5.1 Hz, J=3.7 Hz), 7.36 (d, 2 H, J=3.9 Hz), 7.41 (dd, 2 H, J=3.6 Hz, J=1.1 Hz), 7.51 (dd, 2 H, J=5.1 Hz, J=1.1 Hz), 7.75 (dd, 2 H, J=5.1 Hz, J=1.2 Hz), 7.92 (dd, 2 H, J=3.7 Hz, J=1.2 Hz), 7.94 (d, 2 H, J=3.9 Hz), 8.15 (d, 2 H, J=1.6 Hz), 8.52 (d, 2 H, J=1.6 Hz) ppm. - EI MS (70eV); *m/z* (%): 648 (100) [M^+], 615 (5) [M^+ - SH], 324 (16) [M^{2+}]. - UV/Vis (CH_2Cl_2): 260 nm (4859 $l{\cdot}mol^{-1}cm^{-1}$, lg ε 3.687), 318 nm (5442 $l{\cdot}mol^{-1}cm^{-1}$, lg ε 3.736), 370 nm (5840 $l{\cdot}mol^{-1}cm^{-1}$, lg ε 3.766). - $C_{17}H_{20}N_2S_6$ (648.8): calcd. C 62.94, H 3.11, N 4.32; found C 62.51, H 3.00, N 4.51.

4,4″,6,6″-Tetra-5-thiophen-2-yl-[2,2′,6′,2″]-terpyridine (**6d**): Following the *general procedure* **4d** (488 mg, 500 μmol) and 2-bromo-thiophene **5a** (288 ml, 490 mg, 3.00 mmol) yielded after recrystallization from acetonitrile 119 mg (212 μmol, 42%) of **6d**, colourless crystals, m.p. 274-276°C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3070, 3040, 1585, 1560, 1530, 1505, 1420, 1375, 1220, 840, 805, 735, 685 cm^{-1}. - ^1H NMR (CD_2Cl_2, 400 MHz): δ = 7.21 (dd, 2 H, J=5.1 Hz, J=3.7 Hz), 7.26 (dd, 2 H, J=5.1 Hz, J=3.7 Hz), 7.50 (dd, 2 H, J=5.1 Hz, J=1.2 Hz), 7.55 (dd, 2 H, J=5.1 Hz, J=1.2 Hz), 7.79 (dd, 2 H, J=3.7 Hz, J=1.2 Hz), 7.79 (dd, 2 H, J=3.7 Hz, J=1.2 Hz), 7.95 (d, 2 H, J=1.6 Hz), 8.07 (t, 1H, J=7.8 Hz), 8.65 (d, 2H, J=7.8 Hz), 8.84 (d, 2 H, J=1.6 Hz) ppm. - EI MS (70 eV); m/z (%): 561 (100) [M^+], 528 (14) [M^+ - SH], 478 (3) [M^+ - C_4H_3S], 451 (3) [M^+ - C_4H_3S - HCN], 346 (5) [M^+ - C_4H_3S - C_4H],.319 (9) [M^+ - 2 C_4H_3S - C_5H_2N], 281 (8) [M^{2+}], 242 (2) [M^+ - 2 C_4H_3S - $C_{10}H_5N_2$], 209 (3) [M^+ - 2 C_4H_3S - $C_{10}H_5N_2$ - SH], 184 (2) [M^+ - 2 C_4H_3S - $C_{10}H_5N_2$ - S - C_2H_2], 134 (2) [C_4H_3S-$C_4H_3^+$], 108 (3) [C_4H_3S-C_2H^+]. - $C_{31}H_{19}N_3S_4$ (561.7): calcd. C 66.28, H 3.41, N 7.48; found C 66.36, H 3.60, N 7.45.

6,6′-Di-[2,2′]-bithiophen-5-yl-4,4′-di-(5-octan-1-yl-thiophen-2-yl)-[2,2′]-bipyridine (**6e**): Following the *general procedure* 2-bromo-5-octan-1-yl-thiophene **5b** (415 mg, 1.50 mmol) and **4e** (650 mg, 0.57 mmol) yielded after fcc with CH_2Cl_2 as eluent and recrystallization from acetonitrile : H_2O 2:1 (v/v) 293 mg (0.31 mmol, 54%) of **6e**, yellow solid, m.p. 130-131°C. - IR (KBr): $\tilde{\nu}$ = 3050, 2940, 2900, 2830, 1580, 1560, 1530, 1520, 1450, 1380, 1260, 1230, 1220, 1190, 1100, 1060, 870, 820, 800, 780, 670 cm^{-1}. - ^1H NMR (CD_2Cl_2, 250MHz): δ = 0.92-0.87 (m, 6 H), 1.51-1.20 (m, 20 H), 1.80-1.65 (m, 4 H), 2.87-2.80 (m, 4 H), 6.79 (dt, 2 H, J=3.7 Hz, J=0.8 Hz), 7.06 (dd, 2 H, J=5.0 Hz, J=3.8 Hz), 7.15 (d, 2 H, J=3.8 Hz), 7.27 (dd, 2 H, J=3.6 Hz,

J=1.2 Hz), 7.28 (dd, 2 H, J=4.9 Hz, J=1.2 Hz), 7.43 (d, 2 H, J=3.6 Hz), 7.45 (d, 2 H, J=3.9 Hz), 7.58 (d, 2 H, J=1.6 Hz), 7.83 (t, 1 H, J=7.8 Hz), 8.38 (d, 2 H, J=7.8 Hz), 8.48)d, 2 H, J=1.6 Hz) ppm. - ^{13}C NMR (CD_2Cl_2, 63MHz, DEPT): δ =14.28 (2C, +), 23.12 (2C, -), 29.76 (2C, -), 29.77 (2C, -), 29.86 (2C, -), 30.88 (2C, -), 32.01 (2C, -), 32.35 (2C, -), 113.87 (2C, +), 115.30 (2C, +), 121.51 (2C, +), 124.35 (2C, +), 124.80 (2C, +), 125.07 (2C, +), 125.51 (2C, +), 125.73 (2C, +), 128.38 (2C, +), 129.44 (2C, 0), 138.12 (1C, +), 139.26 (2C, 0), 139.67 (2C, 0), 143.34 (2C, 0), 144.45 (2C, 0), 148.89 (2C, 0), 152.23 (2C, 0), 156.14 (2C, 0). - FD MS (CH_2Cl_2) *m/z* (%) 949 (100) [M^+], 475 (20) [M^{2+}]. UV/Vis (CH_2Cl_2): 328 nm (73206 l·mol^{-1}cm^{-1}, lg ε 4.865), 370 nm (64924 l·mol^{-1}cm^{-1}, lg ε 4.812). - $C_{55}H_{55}N_3S_6$ (950.5): calcd. C 69.50, H 5.83, N 4.42; found C 69.59, H 5.76, N 4.63.

4,4'''-Bis-(5-octan-1-yl-thiophen-2-yl)-6,6'''-di-thiophen-2-yl-[2,2',6',2'',6'',2''']-quaterpyridine (**6f**): Following the *general procedure* **4f** (526 mg, 500 µmol) and 2-bromo-5-octan-1-yl-thiophene **5b** (551 mg, 2.00 mmol) yielded after recrystallization from toluene 308 mg (356 µmol, 72%) of **6f**, colourless crystals, m.p. 188-190°C. - IR (KBr): $\tilde{\nu}$ = 3060, 2950, 2920, 2850, 1590, 1565, 1555, 1540, 1530, 1430, 1420, 1390, 790, 690 cm^{-1}. - ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 0.90 (t, 6 H, J=6.9 Hz), 1.25 - 1.48 (m, 20 H), 1.77 (q, 4H, J=7.5 Hz), 2.92 (t, 4 H, J=7.5 Hz), 6.92 (dd, 2 H, J=3.6 Hz, J=1.0 Hz), 7.20 (dd, 2 H, J=5.1 Hz, J=3.7 Hz), 7.48 (dd, 2 H, J=5.1 Hz, J=1.1 Hz), 7.60 (d, 2 H, J=3.6 Hz), 7.77 (dd, 2 H, J=3.7 Hz, J=1.1 Hz), 7.86 (d, 2 H, J=1.6 Hz), 8.11 (dd, 2 H, J=7.8 Hz, J=7.8 Hz), 8.65 (dd, 2 H, J=7.8 Hz, J=1.1 Hz), 8.71 (d, 2 H, J=1.6 Hz), 8.76 (dd, 2 H, J=7.8, J=1.6 Hz) ppm. - FD MS (CH_2Cl_2); m/z (%): 862 (100) [M^+], 744 (<10) [M^+ - 2 C_4H_9 - 4 H], 431 (<20) [M^{2+}]. - $C_{52}H_{54}N_4S_4$ (863.2): calcd. C 72.35, H 6.31, N 6.49; found C 72.11, H 6.26., N 6.54.

6,6'-Di-[2,2']-bithiophen-5-yl-4,4'-di-anthracen-9-yl-[2,2']-bipyridine (**6g**): Following the *general procedure* 9-bromo-anthracene **5d** (186 mg, 0.19 mmol) and **4c** (256 mg, 0.24 mmol) yielded after recrystallization from DMSO 149 mg (0.18 mmol, 74%) of **6g**, yellow solid, m.p. 209-211°C (decomp.). - IR (KBr): $\tilde{\nu}$ = 3100, 3080, 3060, 1580, 1560, 1510, 1460, 1420, 1380, 1240, 1230, 1200, 1080, 980, 860, 850, 820, 800, 750, 690 cm^{-1}. - ^{1}H NMR (DMSO-d_6, 400MHz, 140°C): δ = 6.98 (dd, 2 H, J=5.1 Hz, J=3.6 Hz), 7.19 (d, 2 H, J=3.9 Hz), 7.21 (dd, 2 H, J=3.6 Hz, J=1.2 Hz), 7.38 (dd, 2 H, J=5.1 Hz, J=1.2 Hz), 7.50-7.64 (m, 18 H), 7.75 (d, 2 H, J=3.9 Hz), 8.01 (d, 2 H, J=1.4 Hz), 8.54 (d, 2 H, J=1.4 Hz) ppm. - EI MS (70 eV) *m/z* (%) 836 (1) [M^+] 418 (100) [M/2$^+$]. - $C_{54}H_{32}N_2S_4$ (837.1): calcd. C 77.48, H 3.85, N 3.25; found C 77.99, H 3.40, N 3.29.

4-[2,2']-Bipyridin-6-yl-6-[2,2']-bithiophen-5-yl-[2,2']-bipyridine (**6h**): Following the *general procedure* 4-bromo-[2,2']-bipyridine **5e** (80 mg, 0.34 mmol) and **4a** (173 mg, 0.28 mmol) yielded after chromatography with CH_2Cl_2 on aluminium oxide 54.5 mg (0.12 mmol, 41%) of **6h**, yellow solid, m.p. 261-265°C. - IR (KBr): $\tilde{\nu}$ = 3120, 3060, 1600, 1570, 1550, 1440, 1420, 1400, 1250, 1110, 1080, 1040, 860, 780, 740, 690 cm^{-1}. - ^1H NMR (DMSO-d_6, 400MHz): δ = 7.16 (dd, 1 H, J=5.1 Hz, J=4.6 Jz), 7.46 (d, 1 H, J=3.9 Hz), 7.50 (dd, 1 H, J=3.6 Hz, J=1.2 Jz), 7.54 (ddd, 1 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.56 (ddd, 1 H, J=7.5 Hz, J=4.8 Hz, J=1.2 Hz), 7.60 (dd, 1 H, J=5.1 Hz, J=1.2 Hz), 8.02 (ddd, 1 H, J=7.9 Hz, J=7.6 Hz, J=1.8 Hz), 8.09 (ddd, 1 H, J=7.9 Hz, J=7.5 Hz, J=1.8 Hz), 8.10 (dd, 1 H, J=5.1 Hz, J=1.9 Hz), 8.15 (d, 1 H, J=3.9 Hz), 8.49 (ddd, 1 H, J=7.9 Hz, J=1.2 Hz, J=1.0 Hz), 8.51 (d, 1 H, J=1.5 Hz), 8.54 (ddd, 1 H, J=7.9 Hz, J=1.2 Hz, J=1.0 Hz), 8.66 (d, 1 H, J=1.5 Hz), 8.79 (ddd, 1 H, J=5.7 Hz, J=1.8 Hz, J=1.0 Hz), 8.80 (ddd, 1 H, J=4.8 Hz, J=1.8 Hz, J=1.0 Hz), 8.87 (dd, 1 H, J=1.9 Hz, J=0.8 Hz), 8.91 (dd, 1 H, J=5.1 Hz, J=0.8 Hz) ppm. - EI MS (70 eV) *m/z* (%) 474 (100) [M^+], 446 (4) [$M^+ - N_2$], 396 (10) [$M^+ - C_5H_4N$], 319 (3) [$M^+ - C_{10}H_7N_2$], 237 (6) [M^{2+}], 156 (2) [$M^+ - C_{18}H_{11}N_2S_2$], 104 (1) [$M^+ - C_{22}H_{14}N_2S_2$], 78 (5) [$M^+ - C_{23}H_{14}N_3S_2$]. - $C_{28}H_{18}N_4S_2$ (474.6): calcd. C 70.86, H 3.82, N 11.80; found C 70.61, H 3.62, N 11.70.

4,4''-Bis-(4-octadecyl-benzoyl)-6,6''-di-5-thiophen-2-yl-[2,2',6',2'']-terpyridine (**6i**): Benzylchlorobis(triphenyl-phosphine)palladium(II) (11.4 mg, 15.0 µmol) was dissolved in 1.5 ml of absolute trichloromethane. First 4-octadecyl-benzoyl chloride **5f** (393 mg, 1.00 mmol) was added and then, after stirring the solution for 5 minutes, **4d** (488 mg, 500 µmol) in 1.5 ml of absolute trichloromethane. The reaction mixture was heated in a sealed tube at 65°C for 50 h. After cooling the precipitate formed was dissolved in chloroform, petroleum ether 40/60 was added and the reaction mixture was kept in a refrigerator for 2 h. The precipitate formed was collected by suction filtration and washed with 10 ml of petroleum ether 40/60. Recrystallization from ethyl acetate yielded 448 mg (412 µmol, 82%) of **6i**, colourless crystals, m.p. 141°C (cloudy liquid), 145-146°C (clear liquid). - IR (KBr): $\tilde{\nu}$ = 3050, 2940, 2910, 2840, 1650, 1640, 1590, 1560, 1535, 1455, 1425, 1380, 1260, 1170, 805, 750, 685 cm^{-1}. - ^1H NMR (CD_2Cl_2, 250 MHz): δ = 0.88 (t, 6 H, J=6.7 Hz), 1.45-1.75 (m, 64 H), 2.67 (t, 4 H, J=7.8 Hz), 7.17 (dd, 2 H, J=5.1 Hz, J=3.7 Hz), 7.32 (AA'BB', 4 H, J=8.5 Hz), 7.50 (dd, 2 H, J=5.1 Hz, J=1.1 Hz), 7.72 (dd, 2 H, J=3.7 Hz, J=1.1 Hz), 7.85 (AA'BB', 4 H, J=8.5 Hz), 7.93 (d, 2 H, J=1.3 Hz), 8.11 (t, 1 H, J=7.8 Hz), 8.63 (d, 2H, J=1.3 Hz), 8.67 (d, 2H, J=7.8 Hz) ppm. - FD MS (toluene); m/z (%): 1110 (100) [M^+], 1082 (<5) [$M^+ - N_2$], 753 (<5) [$M^+ + H - C_{25}H_{41}O$], 658 (<5) [$C_{48}H_{82}^+$], 555 (<5) [M^{2+}]. - $C_{73}H_{95}N_3O_2S_2$ (1110.6): calcd. C 78.94, H 8.62, N 3.78; found C 78.38, H 8.48, N 3.83.

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