### Star-Shaped Tripodal Chemosensors for the Detection of Aliphatic Amines

Susanne Körsten\*<sup>[a]</sup> and Gerhard J. Mohr<sup>[b]</sup>

**Abstract:** In this work, three new tripodal triphenylamine dyes are presented that are capable of reversibly binding amines and diamines to form hemiaminals through a covalent bond. The dyes were synthesized by the Heck reaction and possess stilbene units with one, two, or three trifluoroacetyl groups as receptor moieties. Their interaction with amines and diamines led to changes in their absorption and emission properties, which were detected by UV/Vis and fluorescence spectroscopy. The influence of the number of trifluoroacetyl receptor moieties on the

**Keywords:** amines • chemosensors • fluorescence spectroscopy • Heck reaction • UV/Vis spectroscopy

selectivity and sensitivity of the dyes was studied. Enhanced sensitivity and selectivity for diaminoalkanes was found for the dye we have labeled Tripod-1, with three chemically reactive trifluoroacetyl groups, related to only one or two trifluoroacetyl groups in the dye molecule.

### Introduction

The selective recognition and sensing of neutral analytes, such as amines, alcohols, and saccharides, by artificial receptors is still a challenging field.<sup>[1-3]</sup> The detection of aliphatic amines and diamines is of significant interest as they are widely used as fertilizers, as auxiliaries in dye manufacturing, and in the production of pharmaceuticals. Various amines and diamines are so-called biogenic amines because they are products of the enzymatic decarboxylation of amino acids. Hence, the presence of these amines is indicative of food quality, especially for protein-rich foodstuffs, such as fish or meat.

Several approaches towards selective sensor dyes for amines and diamines, which additionally provide strong optical signal changes in absorbance and fluorescence, have been presented in recent decades. Among them, different receptor groups for amino functions have been used. Tsubaki et al. for instance employed two crown ether units on a phenolphthalein derivative to detect diamines in their ammonium form.<sup>[4,5]</sup> Recently, another ditopic receptor for dia-

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mines was reported by Carofiglio et al. They presented three dimeric metalloporphyrin hosts with tweezer-like structures and observed binding constants in the range from  $4.2 \times 10^6$  to  $3.4 \times 10^7 \text{ m}^{-1}$  for the host-guest interaction of the receptors with a, w-diamines.<sup>[6]</sup> Other indicator dyes exhibited aldehyde moieties as receptors, forming bisiminium ions upon reaction with diamines and producing large changes in fluorescence.<sup>[7]</sup> Lavigne et al. reported on carboxylic acids as receptor units for diamines.<sup>[8,9]</sup> Another possible receptor moiety is the trifluoroacetyl group, which reacts reversibly with amines forming hemiaminals or zwitterions.<sup>[1,10]</sup> To modify the selectivity pattern of the amine recognition, the cooperative effect of the indicator dye plus a structured matrix was evaluated. The preparation of an amine-selective chemosensor with a (trifluoroacetyl)azobenzene reporter group incorporated into a dendrimer was reported by Zimmerman et al.<sup>[11]</sup> Martínez-Máñez et al. used the same chromoreactand for amine detection in hybrid composites.<sup>[12]</sup> They covalently immobilized the sensor dye on mesoporous silica and then embedded this composite into a polymer. The pore size of the silica material and the lipophilic polymer affected the selectivity towards different amines. The approach of using multiple binding sites in one molecule, especially the trifluoroacetyl groups, is another way to enhance the selectivity and sensitivity of the sensor dye. We recently reported on a xanthene dye with two trifluoroacetyl moieties that showed higher selectivity towards diaminoalkanes related to the monofunctionalized xanthene dve.<sup>[13]</sup> The preorganized arrangement of the two receptor groups in one molecule allowed diamine binding through macrocy-



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cle formation and led, therefore, to the observed modified selectivity. A trifluoroacetophenone-based tripodal sensor molecule for the detection of amino acids was developed by Suzuki et al.<sup>[14,15]</sup> They introduced three receptor groups for simultaneous binding of the amino and the carboxylate groups of an amino acid in the anionic form. Another tripodal trifluoroacetophenone derivative for use in ion-selective electrode membranes was presented by Ahn et al.<sup>[16]</sup>

With all this in mind, we decided to develop an optical chemosensor with three trifluoroacetyl groups for amine detection. A triphenylamine core was chosen, which allowed the alignment of three trifluoroacetyl stilbene units. This skeletal structure was employed since triphenylamine is known for its structural rigidity,<sup>[17]</sup> facile convertibility, and strong fluorescence.<sup>[18]</sup> Furthermore, we replaced the three reactive trifluoroacetyl groups with one or two unreactive nitro functions to evaluate substitution effects on selectivity and sensitivity. Thus, we present three new tripodal trifluoroacetyl-functionalized sensor dyes, which can be used as selective and sensitive materials for the detection of aliphatic amines and diamines.

#### **Results and Discussion**

**Synthesis:** By using trisiodotriphenylamine<sup>[19]</sup> (1) as a starting material and 2,2,2-trifluoro-1-(4-vinylphenyl)ethanone, Tripod-1 was synthesized by means of the Heck reaction (Scheme 1).

With the help of structurally related tripodal reference substances, bearing nonreactive nitro groups instead of the trifluoroacetyl groups, the impact of the number of receptor groups in one sensor molecule on the sensitivity and selectivity towards (di)amine detection was evaluated. For this, Tripod-**2** and Tripod-**3** were synthesized, containing one or two nitro group(s) instead of the trifluoroacetyl group, respectively. The nitro group was chosen as it has a similar acceptor strength (Hammett substitution constant  $\sigma_p(-NO_2) =$ 0.78;  $\sigma_p(-COCF_3) = 0.80$ ,<sup>[20]</sup> but no chemical reactivity towards amines. In a precedent Heck reaction of **1** and 4-nitrostyrene, the mono- and dinitrostyrene-substituted compounds **2** and **3** were synthesized and isolated. The subsequent Heck reaction of **2** and **3** with appropriate amounts of 2,2,2-trifluoro-1-(4-vinylphenyl)ethanone, gave the final products Tripod-**2** and Tripod-**3**, respectively (Scheme 2). Tripod-**4** is formed in one reaction step and denotes the nonreactive reference molecule.

**Optical properties**: The amine-sensitive dyes Tripod-1– Tripod-3 and the nonreactive reference dye Tripod-4 were characterized with regards to their optical properties in different solvents. The tripods are soluble in nonpolar and polar organic solvents, such as toluene, dichloromethane, and DMSO. The absorbance maxima ( $\lambda_{max, abs}$ ) of the tripods are all in the range from 445, in nonpolar toluene, to 460 nm, in DMSO (Table 1). An additional absorption band

Table 1. Optical properties of Tripod-1-Tripod-4 in different solvents.

Compound	Solvent	$\lambda_{\max,abs}$ [nm]	$\lambda_{\max,em}$ [nm]	$arPsi_{ m F}$
Tripod-1	toluene	447	517	0.67
-	dichloromethane	454	640	$3.3 \times 10^{-2}$
	DMSO	458	n.d. <sup>[a]</sup>	n.d. <sup>[a]</sup>
Tripod-2	toluene	445	525	0.65
-	dichloromethane	452	615	$5.5 \times 10^{-3}$
	DMSO	460	n.d. <sup>[a]</sup>	n.d. <sup>[a]</sup>
Tripod-3	toluene	445	527	0.65
-	dichloromethane	454	n.d. <sup>[a]</sup>	n.d. <sup>[a]</sup>
	DMSO	461	n.d. <sup>[a]</sup>	n.d. <sup>[a]</sup>
Tripod-4	toluene	443	525	0.66
	dichloromethane	454	n.d. <sup>[a]</sup>	n.d. <sup>[a]</sup>
	DMSO	461	n.d. <sup>[a]</sup>	n.d. <sup>[a]</sup>

[a] No fluorescence determined.

with less intensity is found near 330 nm. Tripod-**1** exhibits high molar absorptivities with log  $\varepsilon$ - values in the range of 4.92 to 4.87. The central nitrogen atom of the triphenylamine core is planar since it has an sp<sup>2</sup>-hybridization.<sup>[21]</sup> The three phenyl rings attached to the nitrogen atom are forced

to assume a propeller-like structure (torsion angle of 41,7°) of the triphenylamine skeleton. As a consequence, the three stilbene side arms are not conjugated to each other, and the absorptivity of each single side arm contributes independently to the global absorptivity of the molecule.

Remarkably, only in toluene do all of the tripods show significant fluorescence, with emission maxima ( $\lambda_{max,em}$ ) at around 520 nm and fluorescence quantum yields ( $\Phi_F$ ) of about 0.65. Weak, or even no fluorescence, was found in more polar di-



Scheme 1. Synthesis of Tripod-1 by means of the Heck reaction.

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Scheme 2. Synthetic routes for Tripod-1-Tripod-4.

chloromethane ( $\lambda_{\max,em} = 615-640 \text{ nm}, \Phi_F < 0.03$ ) and DMSO. These solvent-dependent emission properties are typically observed in the case of donor–acceptor-substituted stilbenes.<sup>[22,23]</sup> The excited state is stabilized by more polar solvents, thus leading to a bathochromic shift of the emission wavelength and additionally to a decrease in emission intensity.

**Reaction with amines and diamines**: The interaction of the new tripodal compounds Tripod-**1**–Tripod-**3** with several amines and diamines in organic solution was investigated. When reacting with amines, the trifluoroacetyl group is reversibly converted into a hemiaminal or a zwitterion (Scheme 3).<sup>[10]</sup>

Accompanied by a decrease in the acceptor strength of the trifluoroacetyl group, the electron delocalization within



Scheme 3. General reaction of trifluoroacetyl groups with primary (a) and secondary (b) amines to form hemiaminals and tertiary amines (c) to form zwitterions.

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the dye molecule is modulated and, therefore, the maxima of absorbance and emission are shifted to shorter wavelengths.<sup>[2]</sup> To study the hemiaminal formation, the primary amine 1-propylamine (PA) and the diami-1,2-diaminoethane noalkanes (DAE), 1,3-diaminopropane (DAP), and 1,4-diaminobutane (DAB) were used. The optical properties of the resulting hemiaminals (HA) are summarized in Table 2. The type of amine we used did not influence the basic optical properties of the formed hemiaminals.

The absorbance maxima of the corresponding HA are around 398 (Tripod-1-HA), 402 (Tripod-2-HA), and 440 nm (Tripod-3-HA) and show negligible solvatochromism. The stepwise addition of amine to a solution of Tripod-1 and subsequent recording of the respective absorbance led to a series

Table 2. Optical properties of the hemiaminals Tripod-**1**-HA–Tripod-**3**-HA resulting from the reaction with PA.

Compound	Solvent	$\lambda_{ m max,abs}$ [nm]	$\lambda_{\max,em}$ [nm]	$arPsi_{ m F}$	$c (PA)^{[c]}$ [mol L <sup>-1</sup> ]
Tripod- <b>1</b> -HA	toluene	396	443	0.80	1.6
	dichloromethane	398	474	0.75	2.5
	DMSO	400	500	0.59	0.03
Tripod-2-HA	toluene	401	445	0.80	0.75
	dichloromethane	403	470	0.75	2.00
	DMSO	404	500	0.59	0.05
Tripod-3-HA	toluene	438 (b) <sup>[a]</sup>	n.d.[b]	n.d. <sup>[b]</sup>	0.75
	dichloromethane	441 (b) <sup>[a]</sup>	n.d. <sup>[b]</sup>	n.d. <sup>[b]</sup>	2.00
	DMSO	450 (b) <sup>[a]</sup>	n.d. <sup>[b]</sup>	n.d. <sup>[b]</sup>	0.05

[a] Broad absorption band. [b] No fluorescence determined. [c] Concentrations of PA were chosen such as to guarantee full conversion of the trifluoroacetyl form into the hemiaminal.

of spectra with three isosbestic points at 310, 360, and 420 nm. As a result of hemiaminal formation, a decrease in absorbance at 460 nm (trifluoroacetyl form) and the simultaneous formation of a new short wavelength maximum (hemiaminal form) near 400 nm was observed (Figure 1).

In the case of Tripod-2 and Tripod-3 and their interaction with amines, the resulting absorbance spectra showed two significant differences relative to Tripod-1. First, the magnitude in signal changes becomes smaller as there are only two, or even only one, trifluoroacetyl group(s) to react with the amine. Second, with increasing numbers of nitro groups in the sensor dye, the hypsochromic shift between the tri-

Chem. Eur. J. 2011, 17, 969-975

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Figure 1. Absorbance spectra of Tripod-1 in DMSO  $(1.18 \times 10^{-5} \text{ M})$  upon the addition of increasing amounts of PA (0-0.03 M). A decrease in absorbance at 460 and 330 nm and an increase at 400 and 290 nm, is observed.

λ [nm]

fluoroacetyl and hemiaminal form is decreased. The unchanged absorption near 450 nm of the nonreactive nitrostilbene side arms upon addition of amine and the absorption band of the hemiaminal form are overlapping so causing a smaller shift in absorbance to shorter wavelengths. Hence the absorbance maxima of Tripod-**2**-HA and Tripod-**3**-HA are in DMSO at 404 and 450 nm, respectively (Figure 2).

The fluorescence maxima of Tripod-1-HA and Tripod-2-HA were similar to each other, ranging from 445 nm in toluene, up to 500 nm in DMSO (Table 2). In contrast to the unreacted trifluoroacetyl derivatives, the corresponding hemiaminals exhibited high quantum yields ( $\Phi_{\rm F}$ =0.59-0.80) in all three solvents. Only Tripod-3-HA did not show any fluorescence in the selected solvents. We assume this is due to the quenching effect of the nitro groups, which are in excess when compared to the trifluoroacetyl/HA groups in Tripod-3. With increasing amounts of 1-propylamine added to a solution of Tripod-1, the fluorescence intensity at 500 nm increases in an off/on mechanism (Figure 3), which indicates the formation of the corresponding hemiaminal Tripod-1-HA. To confirm the nonreactivity of the nitro groups under the measurement conditions, a solution of the reference dye Tripod-4 was exposed to the amines. This showed no changes in absorbance or in fluorescence. Consequently, the nonreactivity of the reference dye was established, as well as the exclusion of pH-dependent changes in absorbance and fluorescence caused by the basic amines.

To evaluate the selectivity of the dyes towards amines and diamines, the respective equilibrium constants were determined according to a procedure previously reported and were compared.<sup>[2,10]</sup>

The selectivity and sensitivity of Tripod-1–Tripod-3 towards monoamines were found to be comparable, only the magnitude in signal changes were smaller depending on the number of receptor groups in the dye molecule. In the case



Figure 2. Absorbance spectra of Tripod-**2** (top) and Tripod-**3** (bottom) in DMSO (each  $1.18 \times 10^{-5}$  M) upon the addition of increasing amounts of PA (0–0.03 M). A decrease in absorbance at 460 nm is observed.



Figure 3. Fluorescence spectra of Tripod-**1** in DMSO  $(1.3 \times 10^{-6} \text{ M}, \text{ excited}$  at 422 nm) upon the addition of increasing amounts of PA (0-0.03 M). The fluorescence intensity of the hemiaminal form at 500 nm increases with increasing amounts of amine added.

of diamine interaction, several results were found. Generally, for the reaction of the tripods with diamines, equilibrium constants were obtained that were one to two decades higher than for monoamines, which demonstrated their higher sensitivity towards diamines (Figure 4).



Figure 4. Equilibrium constants K for the reactions of Tripod-1–Tripod-3 in DMSO with PA and DAE, DAP, and DAB.

Although 1-propylamine showed similar nucleophilicity  $(pK_{b}=3.46)$  in comparison to the diamines  $(pK_{b1}=4.08-$ 3.20), the hemiaminal formation with diamines was favored. The increased sensitivity for diamines is attributed to their ability to form intramolecular hydrogen bonds, as reported by Mertz et al.<sup>[24]</sup> Accordingly, the corresponding hemiaminals are stabilized, which in turn leads to higher equilibrium constants and sensitivities. Furthermore, Figure 4 illustrates the outstanding selectivity of Tripod-1 for DAP. In the case of Tripod-1 and its reaction with diamines, one can observe the following pattern for the equilibrium constants:  $K_{\text{DAE}}$  <  $K_{\text{DAP}} > K_{\text{DAB}}$ . This can be attributed to two main factors. First, according to the diamines' nucleophilicity ( $pK_{b1}$ -(DAE) = 4.08,  $pK_{b1}(DAP) = 3.45$ ,  $pK_{b1}(DAB) = 3.20$ ) one would expect higher equilibrium constants with increasing chain length. Second, the stability of the intramolecular hydrogen bonds is weakened with increasing chain length.<sup>[24]</sup> These two countervailing trends lead to the observed selectivity and can be found for Tripod-2 and Tripod-3. The differences within the tripodal receptors (and the amines) are reflected in the sensitivity ranges, which are given for PA and DAP in Table 3. Noteworthy are the up to 75-fold higher sensitivities of all tripods towards DAP in comparison to PA.

Comparing the sensor dyes Tripod-1–Tripod-3, and their interaction with amines and diamines, several observations were made. First, Tripod-1–Tripod-3 showed comparable equilibrium constants for the reaction with PA (mono-amine). Second, for the reaction with diamines, the equilibrium constants are significantly increased when compared with the results for PA. The higher selectivity and sensitivity towards diamines is based on the stabilization of the result-

Table 3. Sensitivity range of Tripod-1-Tripod-3 in DMSO towards 1	PA
and DAP, corresponding to the quasi-linear part of the sigmoidal	re-
sponse curve.	

Compound	Highest se	nsitivity range
	РА [тм]	DAP [µм]
Tripod-1	0.3-6.0	6-60
Tripod-2	0.3–2.5	10-316
Tripod-3	0.6–2.5	18–316

ing hemiaminals by intramolecular hydrogen bonds. For each single tripod the selectivity is highest for DAP and lowest for DAB. On the one hand, the increasing chain length leads to less stabilization of the hemiaminals through hydrogen bonds. However, the longer the diamine chain, the higher the nucleophilicity of the respective amine group. With this is mind, the highest sensitivity for DAP is not surprising. When comparing the reactions of Tripod-1–Tripod-3 with diamines, the higher selectivity for Tripod-1 over Tripod-2 and Tripod-3 is observed due to the higher amount of receptor groups within the dye molecule. More trifluoroacetyl groups statistically favor the reaction with the amine close to the dye molecule.

With multiple binding sites, Tripod-**1** and Tripod-**2** are theoretically assumed to form intramolecularly bridged hemiaminals with diamines (see our previous publication on a trifluoroacetyl-functionalized xanthene dye<sup>[13]</sup>). However, for this study there are two reasons why bridged hemiaminals are not observed. Due to the rigidity of the tripodal structures, the side chains and therefore the receptor groups are impeded to converge. Furthermore, the chain length of the diamines used is not long enough to fit between two receptor groups without causing great sterical strain to the tripodal structure. Semiempirical PM3 calculations verify that there is too much strain on two side chains to afford an intramolecular and bridged binding of the diamines.

#### Conclusion

In this work, three new tripodal triphenylamine dyes are presented that are capable of reversibly binding amines and diamines to form hemiaminals through a covalent bond. The dyes bear stilbene units with one, two, or three trifluoroacetyl groups as receptor moieties attached to them. The hemiaminal formation leads to changes in absorption and emission of the sensor dyes, which are detectable with UV/Vis and fluorescence spectroscopy. Enhanced sensitivity and selectivity for diaminoalkanes was found when three chemically reactive trifluoroacetyl groups were introduced into the tripodal stilbene moiety, related to only two or one trifluoroacetyl groups. Our ongoing research is focused on the interaction of these tripodal structures with amino acids. Preliminary tests show high selectivity and sensitivity towards these analytes, which is significantly dependent on the number of reaction sites.

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#### **Experimental Section**

**Reagents**: Chemicals were purchased from Fluka and Aldrich and were used without any further purification. All solvents and amines used were of analytical reagent grade.

**Apparatus**: The absorbance spectra of dissolved dyes were recorded on a Perkin–Elmer Lambda 16 spectrometer. Absorption measurements were performed by using quartz cuvettes with the respective dye solution. Fluorescence measurements were performed on a Fluorolog 3 spectrometer from Jobin Yvon-Spex. NMR spectra were recorded on Bruker AC-250 or DRX-400 apparatus. The quantum yields were determined on a LS50B from Perkin–Elmer by using quinine sulfate in a 0.1 N H<sub>2</sub>SO<sub>4</sub> solution. Mass spectra were obtained on a MAT SSQ 710 and on MAZ95XL from Finnigan.

#### Synthesis

Synthesis of tris(4-iodophenyl)amine (1): Triphenylamine (0.5 g, 2.04 mmol), HgO (2.06 g, 9.52 mmol), and iodine (2.59 g, 10.2 mmol) were dissolved in ethanol (30 mL) and stirred overnight at room temperature. Afterwards, the solvent was removed in vacuum. The solid residue was redissolved in toluene (30 mL) and refluxed. The solution was filtered through a short column of Al<sub>2</sub>O<sub>3</sub> and the final product was precipitated with methanol. Yield: 1.04 g (1.67 mmol, 82%); <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta = 7.53$  (d,  ${}^{3}J(H,H) = 8.7$  Hz, 6H), 6.80 ppm (d,  ${}^{3}J(H,H) = 8.4$  Hz, 6H);  ${}^{13}C$  NMR (62.9 MHz, CDCl<sub>3</sub>, 25 °C, TMS): δ=86.57 (CI), 126.0 (NCC), 138.45 (ICC), 146.57 ppm (NC); MS (DEI): m/z: 622.8 [ $M^+$ ]; elemental analysis calcd (%) for C<sub>18</sub>H<sub>12</sub>I<sub>3</sub>N: C 34.70, H 1.94, N 2.25, I 61.11; found: C 34.99, H 1.80, N 2.20, I 61.08. Synthesis of Tripod-1: Tris(4-iodophenyl)amine (1) (0.5 g, 0.8 mmol), 2,2,2-trifluoro-1-(4-vinylphenyl)ethanone (0.67 g, 3.3 mmol), dry THF (5 mL), triethylamine (5 mL), and [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (35 mg, 0.057 mmol) were added to a heavy-walled reaction chamber and tightly closed. The mixture was heated up to 115°C for 55 h. After cooling, water was added and the reaction mixture was extracted three times with dichloromethane. The combined organic phase was dried over magnesium sulfate, filtered, and evaporated to dryness. The resulting crude product was purified by column chromatography (hexane/dichloromethane 3:1) to give (160 mg, 0.18 mmol, 12%) Tripod-1. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, 25°C, TMS):  $\delta = 7.07$  (d, 3H), 7.16 (d, 6H), 7.28 (d, 3H), 7.50 (d, 6H), 7.65 (d, 6H), 8.07 ppm (d, 6H); MS (DEI): m/z: 838 [M<sup>+</sup>-H]; elemental analysis calcd (%) for  $C_{48}H_{30}F_9NO_3{:}\ C$  68.65, H 3.60, N 1.67; found: C 68.85, H 3.55, N 1.51.

Synthesis of compound 2, compound 3, and Tripod-4: Compound 1 (1.04 g, 1.67 mmol), 4-nitrostyrene (0.54 g, 3.62 mmol), THF (10 mL), triethylamine (3.5 mL), and [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.07 g, 0.1 mmol) were reacted as described above for 48 h at 85 °C. The resulting crude product was purified by column chromatography with increasing solvent polarity by using a hexane/ethyl acetate mixture (from 5:1 to 1:1) to give the three products in the following yields: Compound 2 (130 mg, 0.20 mmol), compound 3 (150 mg, 0.23 mmol), and Tripod-4 (200 mg, 0.29 mmol).

Compound **2**: <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 6.85$  (d, <sup>3</sup>*J*-(H,H) = 8.75 Hz, 4H), 7.08 (m, 2H), 7.15 (d, <sup>3</sup>*J*(H,H) = 16.3 Hz, 1H), 7.28 (d, <sup>3</sup>*J*(H,H) = 16.3 Hz, 1H), 7.40 (m, 2H), 7.58 (d, <sup>3</sup>*J*(H,H) = 8.75 Hz, 4H), 7.64 (m, 2H), 8.22 ppm (m, 2H); <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 86.6$  (CI), 123.7 (NCC), 124.1 (NCC), 126.0 (*C*=C), 126.6 (NCCC), 126.9 (*C*CNO<sub>2</sub>), 127.0 (*C*=C), 129.0 (*C*CCNO<sub>2</sub>), 138.2 (NCCC), 138.5 (NC), 143.9 (*C*=CC), 146.6 (NC), 146.8 (NCCCC), 147.3 ppm (*C*NO<sub>2</sub>); MS (DEI): *m*/*z*: 644 [*M*<sup>+</sup>], 614 [*M*<sup>+</sup>-NO], 518 [*M*<sup>+</sup> -I].

*Compound* **3**: <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 6.91$  (d, <sup>3</sup>*J*-(H,H) = 8.7 Hz, 2H), 7.05 (d, <sup>3</sup>*J*(H,H) = 16.7 Hz, 2H), 7.1 (d, <sup>3</sup>*J*(H,H) = 8.8 Hz, 4H), 7.23 (d, <sup>3</sup>*J*(H,H) = 16.7 Hz, 2H), 7.46 (d, <sup>3</sup>*J*(H,H) = 8.8 Hz, 4H), 7.59 (d, <sup>3</sup>*J*(H,H) = 8.7 Hz, 2H), 7.61 (m, <sup>3</sup>*J*(H,H) = 8.7 Hz, 4H), 8.22 ppm (m, <sup>3</sup>*J*(H,H) = 16.7 Hz, 4H); <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta = 86.95$  (CI), 123.7 (NCC), 124.1 (CCNO<sub>2</sub>), 125.1 (C=C), 126.6 (CCCNO<sub>2</sub>), 128.1 (NCCC), 131.3 (NCCCC), 132.4 (*C*=C), 138.5 (*CC*I), 143.9 (CNO<sub>2</sub>), 146.6 (C=CC), 146.6 (NC), 147.3 ppm (NC); MS (DEI):

*m*/*z*: 665.1 [*M*<sup>+</sup>], 635.2 [*M*<sup>+</sup>-NO], 605 [*M*<sup>+</sup>-2NO], 539.4 [*M*<sup>+</sup>-I], 509.3 [*M*<sup>+</sup>-I-NO], 479.3 [*M*<sup>+</sup>-I-2NO].

*Tripod-4*: <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 7.15 (d, <sup>3</sup>*J*-(H,H) = 8.5 Hz, 6H), 7.48 (d, <sup>3</sup>*J*(H,H) = 8.5 Hz, 6H), 7.07 (d, <sup>3</sup>*J*(H,H) = 16.26 Hz, 3H), 7.25 (d, <sup>3</sup>*J*(H,H) = 16.26 Hz, 3H), 7.62 (d, <sup>3</sup>*J*(H,H) = 8.75 Hz, 6H), 8.22 ppm (d, <sup>3</sup>*J*(H,H) = 8.75 Hz, 6H); <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>, 25 °C, TMS): 124.2 (CCNO<sub>2</sub>), 124.4 (NCC), 125.2 (C=C), 126.6 (CCCNO<sub>2</sub>), 128.2 (NCCC), 131.5 (NCCCC), 132.4 (C=C), 143.9 (CNO<sub>2</sub>), 146.6 (C=CC), 147.3 ppm (NC); MS (DEI): *m*/*z*: 686 [*M*<sup>+</sup>], 656 [*M*<sup>+</sup> -NO]; elemental analysis calcd (%) for C<sub>42</sub>H<sub>30</sub>N<sub>4</sub>O<sub>6</sub>: C 73.46, H 4.40, N 8.16; found: C 73.78, H 4.24, N 7.80.

Synthesis of Tripod-2: Compound 2 (0.11 g, 0.17 mmol), 2,2,2-trifluoro-1-(4-vinylphenyl)ethanone (0.2 g, 1.0 mmol), THF (7 mL), triethylamine (7 mL), and [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.01 g) were reacted as described above for 48 h at 80 °C. After extraction with dichloromethane and evaporation of the solvent, the resulting crude product was purified by column chromatography with increasing solvent polarity by using a hexane/dichloromethane mixture (from 5:1 to 2:1) to give Tripod-2 (30 mg, 0.04 mmol, 22 % yield). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$  = 7.08 (d, <sup>3</sup>*J*(H,H) = 16.4 Hz, 3 H), 7.15 (d, <sup>3</sup>*J*(H,H) = 8.63 Hz, 2H), 7.16 (d, <sup>3</sup>*J*(H,H) = 8.6 Hz, 4H), 7.25 (d, <sup>3</sup>*J*(H,H) = 16.4 Hz, 3H), 7.50 (m, 6H), 7.65 (d, <sup>3</sup>*J*(H,H) = 8.6 Hz, 2 H), 7.66 (d, <sup>3</sup>*J*(H,H) = 8.6 Hz, 4 H), 8.08 (m, 4H), 8.23 ppm (m, 2H); MS (DEI): *m*/*z*: 788 [*M*<sup>+</sup>], 757 [*M*<sup>+</sup>-NO].

Synthesis of Tripod-3: Compound 3 (0.1 g, 0.15 mmol), 2,2,2-trifluoro-1-(4-vinylphenyl)ethanone (0.12 g, 0.6 mmol), THF (6 mL), triethylamine (5 mL), and [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.05 g) were reacted as described above for 24 h at 65 °C. After extraction with dichloromethane and evaporation of the solvent, the resulting crude product was purified by column chromatography with increasing solvent polarity by using a hexane/dichloromethane mixture (from 5:1 to 2:1) to give Tripod-3 (40 mg, 0.05 mmol, 36% yield). <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>, 25 °C, TMS):  $\delta$ =7.07 (d, <sup>3</sup>*J*(H,H) = 16.26 Hz, 3 H), 7.16 (d, <sup>3</sup>*J*(H,H)=8.6 Hz, 6H), 7.25 (d, <sup>3</sup>*J*(H,H) = 8.6 Hz, 6H), 7.62 (d, <sup>3</sup>*J*(H,H)=16.28 Hz, 1H), 7.49 (d, <sup>3</sup>*J*(H,H)=8.6 Hz, 6H), 7.62 (d, <sup>3</sup>*J*(H,H)=7.8 Hz, 2H), 8.22 ppm (d, <sup>3</sup>*J*(H,H)=8.83 Hz, 4H); MS (DEI]: *m*/z: 737 [*M*<sup>+</sup>], 707 [*M*<sup>+</sup>-NO]; elemental analysis calcd (%) for C<sub>44</sub>H<sub>30</sub>F<sub>3</sub>N<sub>3</sub>O<sub>5</sub>: C 71.64, H 4.10, N 5.70; found: C 71.32, H 4.26, N 5.41.

#### Acknowledgements

This work was supported by the project MO 1062/3-1, MO 1062/5-1, and MO 1062/6-1 of the Deutsche Forschungsgemeinschaft, and also by the Bayerische Staatsministerium für Wirtschaft, Infrastruktur, Verkehr und Technologie within project AZ-Nr.: 20.10-3410-2 (Projekt Sensormaterialien). This support is gratefully acknowledged. We thank R. Martínez-Máñez, S. C. Zimmerman, and D. Weiß for stimulating discussions. We also thank H. Müller for performing fluorescence measurements and C. Cranfield for correcting the manuscript.

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Received: March 29, 2010

Revised: July 12, 2010

Published online: November 19, 2010