Supporting Information

1. Instrumentation

^{1}H-NMR and ^{13}C-NMR spectroscopy were performed on a Varian Mercury spectrometer (400 MHz) in deuterated solvents (CD_2Cl_2 or CD_3CN) at 25 °C, using TMS as internal standard.

Matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-ToF MS) was carried out on a Voyager-DE PRO biospectrometry workstation (Applied Biosystems), with α-cyano-hydroxycinnamic acid as matrix.

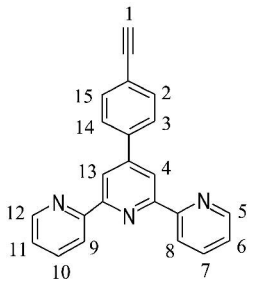
Elemental analyses were obtained on a EuroVector EuroEA3000 elemental analyser for CHNS-O.

2. Synthesis of the supramolecular units and complexes

4'-(4-Ethynyl-phenyl)-2,2':6',2"-terpyridine.[41] 4-Ethynylbenzaldehyde (1.69 g, 12.9 mmol) was dissolved in EtOH (60 mL). Subsequently, 2-acetylpyridine (3.15 g, 25.9 mmol), powdered KOH (1.07 g, 25.9 mmol) and aqueous NH_3 (25%, 40 mL) were added to the solution. After stirring the mixture for 4 h at room temperature the precipitate was filtered off and washed with EtOH (3 × 10 mL). The crude product was purified by recrystallization from ethanol.

Yield: 1.48 g (44%), yellowish powder.

^{1}H-NMR (400 MHz, CD_2Cl_2) δ/ppm = 3.27 (s, 1H, 1), 7.37-7.41 (m, 2H, 6, 11), 7.66-7.68 (m, 2H, 2, 15), 7.88-7.94 (m, 4H, 3, 7, 10, 14), 8.68-8.74 (m, 4H, 5, 8, 9, 12), 8.77 (s, 2H, 4, 13).



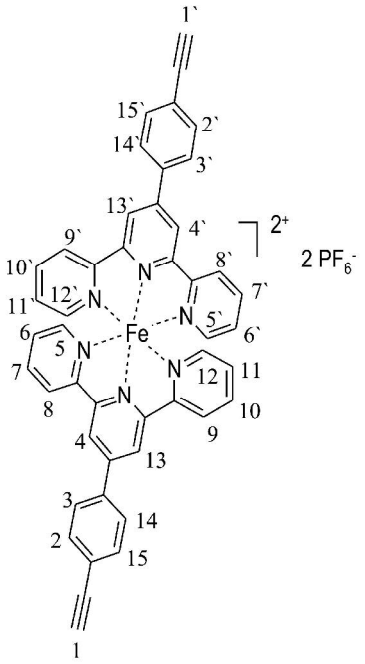
^{13}C-NMR (100 MHz, CD_2Cl_2): δ/ppm = 78.4, 83.1, 118.5, 121.1, 122.7, 123.9, 127.2, 132.7, 136.8, 138.9, 149.1, 149.1, 155.9, 156.1.

Fe(II) *bis*[4'-(4-ethynylphenyl)-2,2':6',2''-terpyridine] complex (1).

A mixture of 4'-(4-ethynylphenyl)-2,2':6',2''-terpyridine (50 mg, 0.15 mmol) and $Fe(OAc)_2$ (12.18 mg, 0.07 mmol) in $CHCl_3$ (0.5 mL) and CH_3CN (1 mL) was refluxed for 12 h. During this time the solution turned purple. A 10-fold excess of NH_4PF_6 (114 mg) was added to the solution and the mixture was refluxed for an additional hour. The crude product was precipitated by cooling down the reaction mixture. Further purifications were performed by washing the product with deionized water followed by recrystalization from diethyl ether. The final product was dried in vacuum.

Yield: 51 mg (70%).

^{1}H-NMR (400 MHz, CD_3CN): δ/ppm = 3.71 (s, 2H, 1, 1`), 7.19 (dd, 4H, $^{4}J$ = 3.2, $^{3}J$ = 6.2 Hz, 6, 6`, 11, 11`), 7.19 (d, 4H, $^{3}J$ = 5.2 Hz, 5, 5`, 12, 12`), 7.93 (m, 8H, 2, 2`, 7, 7`, 10, 10`, 15, 15`), 8.34 (d, 4H, $^{3}J$ = 9.2 Hz, 3, 3`, 16, 16`), 8.63 (d, 4H, $^{3}J$ = 8 Hz, 8, 8`, 9, 9`), 9.20 (s, 4H, 4, 4`, 13, 13`).



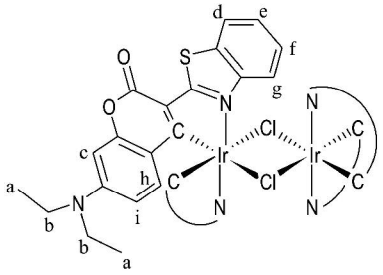
Elem. anal. calcd. for $FeC_{46}H_{30}N_6P_2F_{12}$ (1012.51): C, 54.56%; H, 2.98%; N, 8.30%. Found: C, 54.31%; H, 3.30%; N, 8.16%.

UV-Vis (CH_3CN): λ_{max} ($\varepsilon/10^6$ $L \cdot mol^{-1} \cdot cm^{-1}$) = 285 (5.02), 320 (5.35), 570 (2.20).

***Tetrakis*(3-(2-benzothiazolyl)-7-(diethylamino)coumarinato-N,C4')(μ-dichloro) diiridium (2).** Iridium(III) trichloride hydrate (412 mg, 1.17 mmol) and coumarin 6 (1.19 mg, 3.4 mmol) were added to a degassed mixture of 2-ethoxyethanol (30 mL) and water (10 mL). After refluxing for 24 h under a slight argon stream, the suspension was cooled to room temperature, and the precipitate was filtrated, washed with distilled water and dried. A solution of the crude product in dichloromethane was filtered by using a glass filter frit. The final purification was achieved by two precipitation steps in ethyl acetate.

Yield: 769 mg (73%), red powder.

^{1}H-NMR (400 MHz, CD_2Cl_2): δ/ppm = 0.82 (t, 24H, ^{3}J = 7.00 Hz, a), 2.94-3.09 (m, 16H, b), 4.88-4.90 (m, 4H, h), 5.23-5.28 (m, 4H, i), 6.03-6.04 (m, 4H, c), 6.94-7.01 (m, 8H, e, f), 7.27-7.30 (m, 4H, g), 7.75-7.78 (m, 4H, d).



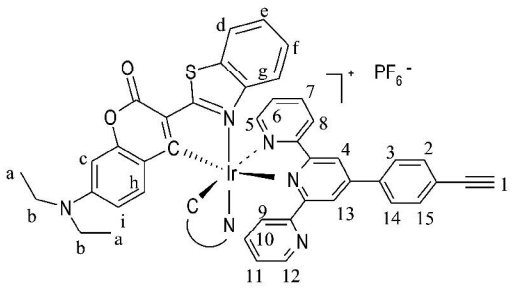
^{13}C-NMR (100 MHz, CD_2Cl_2): δ/ppm = 12.41, 45.00, 96.25, 108.59, 117.99, 119.25, 122.83, 123.08, 124.18, 127.35, 129.94, 131.69, 150.44, 151.668, 154.07, 157.38, 176.33, 178.70.

Elem. anal. calcd. for $Ir_2C_{80}H_{68}O_8N_8S_4Cl_2$ (1853.08): C, 51.85%; H, 3.70%; N, 6.05%; S, 6.92%. Found: C, 51.77%; H, 3.81%; N, 5.80%; S, 6.52%.

***Bis*(3-(2-benzothiazolyl)-7-(diethylamino)coumarinato-C^2,N´)(4'-(4-ethynyl-phenyl)-2,2':6',2"-terpyridine) iridium hexafluorophosphate (3).** *Tetrakis*(3-(2-benzothiazolyl)-7-(diethylamino)coumarinato N,C4')(μ-dichloro)diiridium (**2**) (30 mg, 0.016 mmol) and 4'-(4-ethynyl-phenyl)-2,2':6',2"-terpyridine (10.79 mg, 0.032 mmol) were added to a degassed mixture of MeOH (4 mL) and CH_2Cl_2 (8 mL); the mixture was refluxed under Ar for 4 h. Afterwards the solution was cooled to room temperature, an excess of NH_4PF_6 (100 mg) was added and the mixture was stirred overnight at room temperature. Evaporation of the solvents resulted in the crude product. To remove the excessive amount of ammonium salt, the complex was dissolved in CH_2Cl_2 (20 mL) and

extracted with water (3 × 20 mL), followed by drying over $MgSO_4$. The solution was filtered, concentrated to a volume of 2 mL and precipitated in pentane.

Yield: 12.7 mg (32%), red-orange solid.



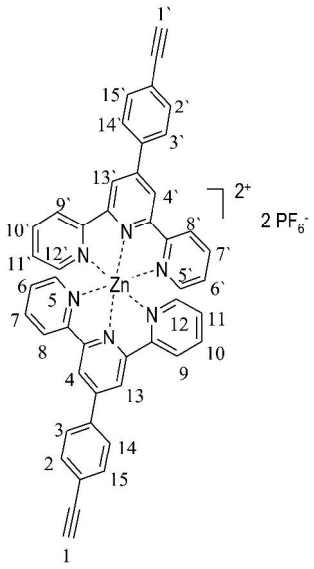
^{1}H-NMR (400 MHz, CD_2Cl_2) δ/ppm = 1.06 (t, 6H, ^3J = 7.0 Hz, a/a`), 1.15 (t, 6H, $^3J$ = 7.2 Hz, a/a`), 3.25-3.41 (m, 8H, b/b`), 3.43 (s, 1H, 1), 5.82-5.84 (dd, 1H, $^3J$ = 9.6 Hz, $^4J$ = 2.8 Hz, i/i`), 5.91-6.06 (m, 4H, d/d`, h, h`, i/i`), 6.19 (d, 1H, $^4J$ = 2.4 Hz, c, c`), 6.32 (d, 1H, ^4J = 2.8 Hz, c/c`), 6.85-6.89 (m, 1H, 7), 7.05-7.16 (m, 2H, 8, e/e`), 7.19-7.25 (m, 1H, e/e`), 7.29-7.34 (m, 2H, d/d`, f/f`), 7.37-7.41 (m, 1H, f/f`), 7.52-7.56 (m, 1H, 10), 7.67-7.69 (m, 2H, 2/3/14/15), 7.77-7.93 (m, 2H, 2/3/14/15), 7.86-7.97 (m, 4H, 6, 4/13, g, g`), 8.12-8.14 (m, 1H, 5), 8.22-8.30 (m, 2H, 9, 11), 8.56-8.57 (m, 1H, 4/13), 8.62-8.69 (m, 1H, 12).
UV/vis (CH_2Cl_2): λ_{max} (ε/10^6 L·mol^{-1}·cm^{-1}) = 310 (3.59), 466 (7.18), 486 (8.09).
MALDI-TOF MS: *m/z*: 1224.12 $[C_{63}H_{49}S_2O_4N_7Ir– PF_6]^+$

Zn(II) *bis*[4'-(4-ethynylphenyl)-2,2':6',2''-terpyridine] complex (4).

A mixture of 4'-(4-ethynylphenyl)-2,2':6',2''-terpyridine (50 mg, 0.15 mmol) and $Zn(OAc)_2$ (12.8 mg, 0.07 mmol) in $CHCl_3$ (0.5 mL) and CH_3CN (1 mL) was refluxed for 12 h. A 10-fold excess of NH_4PF_6 (114 mg) was added to the solution and refluxing was continued for 1 hour. The crude product precipitated by cooling the reaction mixture to room temperature. Further purification was performed by washing the crude product with deionized water followed by recrystallization from methanol. The final product was dried in vacuum.

Yield: 51.3 mg (60%), pale yellow powder.

^{1}H-NMR (400 MHz, CD_3CN): δ/ppm = 3.69 (s, 2H, 1, 1`), 7.42 (dd, 4H, $^3J$ = 5.8 Hz, $^4J$ = 2.6 Hz, 6, 6`, 11, 11`), 7.85 (d, 4H, $^3J$ = 4.9 Hz, 5, 5`, 12, 12`), 7.89 (d, 4H, $^3J$ = 8.5 Hz, 2, 2`, 15, 15`), 8.20 (m, 8H, 3, 3`, 7, 7`, 10, 10`, 14, 14`), 8.73 (d, 4H, $^3J$ = 8 Hz, 8, 8`, 9, 9`), 8.99 (s, 4H, 4, 4`, 13, 13`).



Elem. anal. calcd. for $ZnC_{43}H_{30}N_6P_2F_{12}$ (1022.04): C, 54.05%; H, 2.96%; N, 8.22%. Found: C, 53.92%; H, 2.98%; N, 8.15%.

UV-Vis (CH_3CN): λ_{max} ($\varepsilon/10^6$ L·mol^{-1}·cm^{-1}) = 234 (3.45), 287 (4.31), 311 (3.58), 326 (3.30), 338 (2.76).

3. Characterization of the surfaces

3.1. FT-IR spectroscopy

For the characterization of the reactions on substrates grazing angle FT-IR was utilized. Figure S1 displays the IR spectra of the modified monolayers after each modification step. Because the positions of the $–CH_2$ stretching vibrations provide information about the quality of the monolayer the precursor layer can be analyzed by FT-IR spectroscopy.

The asymmetric and symmetric vibrations for the 11-bromoundecyltrichlorosilane monolayer on silicon were located at 2927 and 2855 cm^{-1}, respectively (Figure S1a). After the conversion of bromine to azide the positions of the $–CH_2$ vibrations remain at 2927 and 2855 cm^{-1} and the intensities of the peaks are comparable; this indicates that the monolayer is not degraded during the reaction (Figure S1b). At 2100 cm^{-1} a characteristic absorption peak for the azide functionality appears, which was not visible for the bromine terminated SAM. After cycloaddition of the Fe(II) complex (**1**) the absorption peak at 2100 cm^{-1} disappears completely (Figure S1c). The vibrations for the $-CH_2$ vibrations remain at 2926 and 2855 cm^{-1}.

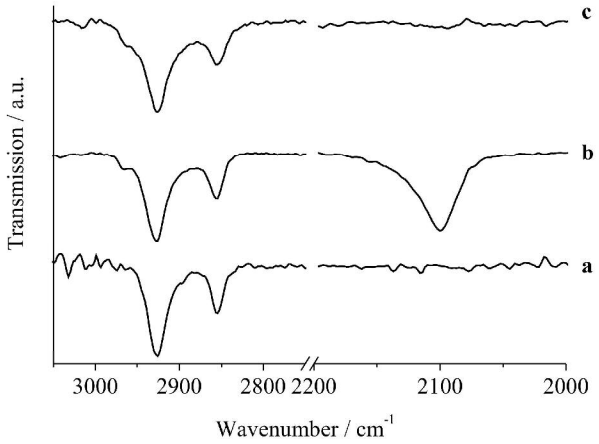


Figure 1: IR spectra of (a) the bromine, (b) the azide and (c) the clicked SAM with (**1**).

3.2. XPS spectroscopy

High resolution XPS investigations were performed on silicon/glass substrates to quantify the chemical reactions (Figure S2). Special emphasis was placed on the investigation of the Br(3d) and N(1s) regions of the spectra. The bromine terminated monolayer (Figure S2, left, (a)) revealed a strong peak at 71 eV, which was assigned to the Br(3d) signal, and thus proved the presence of bromine in the precursor layer. After nucleophilic substitution to azide this peak disappeared completely (Figure S2, left, (b)), indicating the quantitative conversion of the bromine functions of the monolayer. At 401 and 405 eV a split-peak in the N(1s) region is present for the azide functionalities (Figure 2, right, (b)). For the bromine terminated monolayer no nitrogen peak was observed (Figure S2, right, (a)). The splitting of the peak indicates the presence of two nitrogen species present in the azide terminated monolayer, reflecting the two differently charged nitrogen atoms. After cycloaddition of the Fe(II) *bis*-terpyridine complex the splitting of the N(1s) signal disappears and one single peak remains, indicating a successful conversion (Figure S2, right, (c)).

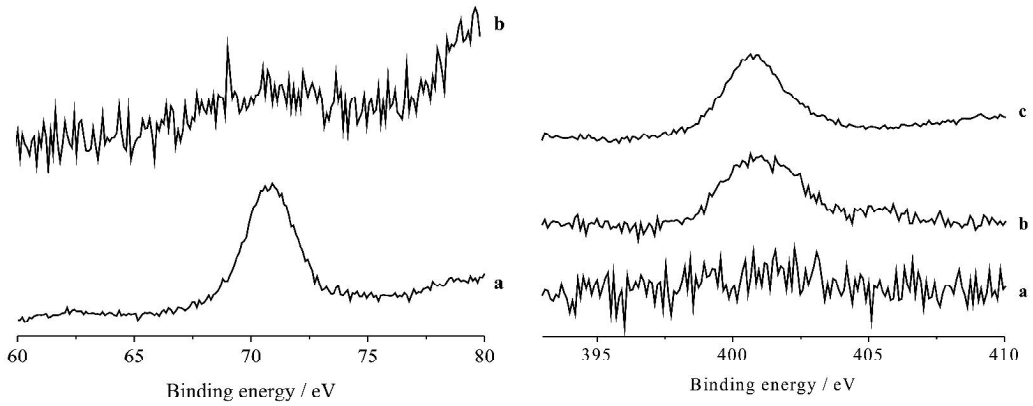


Figure 2: Left: XPS spectra of the Br(3d) region. Right: XPS spectra of the N(1s) region. (a) The bromine, (b) the azide and (c) the clicked SAM with (**1**).

4. Reaction conditions for the 1,3-dipolar cycloaddition of the azide terminated substrates and the Fe(II) complex (1)

A catalytic amount of $CuSO_4 \times 5\ H_2O$ and sodium ascorbate is not sufficient to obtain a quantitative conversion of the azide and the acetylene functionalized Fe(II) *bis*-terpyridine complex (**1**). Therefore a different catalyst was chosen. An excess of CuI leads, after increasing the reaction time from 24 to 48 h, to a quantitative conversion of the azide functionalities.

time (h)[a]	catalyst	amount of catalyst	dissolution of catalyst in water	quantitative conversion
24	$CuSO_4 \times 5\ H_2O$[b]	5 mol%	in 1 mL of water	no
24	$CuSO_4 \times 5\ H_2O$[b]	5 mol%	no	no
24	CuI	excess	no	no
48	CuI	excess	no	yes

[a] temperature: 80 °C; [b] reducing agent: sodium ascorbate