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Diazocine functionalized TATA Platforms

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Abstract

Recently, it has been shown that the thermochemical *cis→trans* isomerization of azobenzenes is accelerated by a factor of more than 1000 by electronic coupling to a gold surface via a conjugated system with 11 bonds and a distance of 14 Å. The corresponding molecular architecture consists of a platform (triazatriangulenium (TATA)) which adsorbs on the gold surface, with an acetylene spacer standing upright, like a post in the middle of the platform and the azobenzene unit mounted on top. The rate acceleration is due to a very peculiar thermal singlet-triplet-singlet mechanism mediated by bulk gold. To investigate this mechanism further and to examine scope and limitation of the “spin-switch catalysis” we now prepared analogous diazocine systems. Diazocines, in contrast to azobenzenes, are stable in the *cis* configuration. Upon irradiation with light of 405 nm the *cis* configuration isomerizes to the *trans* form, which slowly returns back to the stable *cis* isomer. To investigate the thermal *trans→cis* isomerization as a function of the conjugation to the metal surface, we connected the acetylene spacer in *meta* (weak conjugation) and in *para* (strong conjugation) position. Both isomers form ordered monolayers on Au(111) surfaces.

Keywords

Diazocine, TATA Platform, self-assembled monolayers, *cis*-*trans* isomerization, photochrome

Introduction

Catalysts increase chemical reaction rates by lowering the activation energies and thus create more favorable reaction pathways.[1-4] However, there are very few reactions which do not follow classical Eyring theory.[5,6] The rate of these reactions is not dependent on an activation barrier but controlled by quantum mechanical transition probabilities between two quantum states.[7-10] The majority of these quantum chemically forbidden reactions are photochemical processes or transition metal reactions including transitions between spin states or electronic states. We recently discovered a purely organic system in the ground state, whose reaction rate is accelerated from days to seconds by electronic coupling to a bulk gold surface via a conjugated linker over 11 bonds and 14 Å.[11] Thermal *cis*→*trans* isomerizations of azobenzenes are usually slow with half-lives of the *trans* isomer within the range of hours to days at room temperature (parent azobenzene: 4-5 d at 25°C).[12] Rotation around the N=N bond is a symmetry forbidden process and the slow isomerization proceeds via inversion at the N atoms.[13] The rate of isomerization is temperature dependent and follows a classical Arrhenius type behavior.[12] However, the rate and the mechanism change dramatically if the azobenzenes are electronically coupled to bulk gold.[14-17] To investigate the *cis*→*trans* isomerizations of azobenzenes as a function of electronic coupling systematically, we used the so-called platform approach.[18] The azobenzenes are not directly adsorbed on the surface, but covalently mounted on “TATA” (triazatriangulenium) platforms which adsorb on Au(111) surfaces. A spacer, such as an ethynyl group is connected to the central carbon atom like a post and the azobenzene is mounted on top of the spacer. After preparation of an ordered self-assembled monolayer on gold, the azobenzene units are freestanding upright on the surface. The platform defines the lateral distance between next neighbors and provides the free volume for unhindered isomerization of the azobenzene units.[19-20] The length and electronic nature of the spacer units control the distance from the surface and define the electronic coupling with the metal surface.[11,18] With increasing π conjugation from the azobenzene into the platform, and thus coupling to the gold surface, the activation barrier drops to almost zero (~8 kJ mol^{-1}) and the frequency factors (logA) become negative.[11] Vanishing barriers and low frequency factors are typical for non-adiabatic reactions.[9] The mechanism was elucidated as a singlet-triplet-singlet spin change process, which is forbidden in solution but mediated by coupling to the conduction band of the bulk gold. We are now exploring scope and limitations of this peculiar spin catalysis. To investigate if the reverse isomerization process from the *trans* to the *cis* configuration would also be accelerated, and to further scrutinize the coupling effects, we prepared analogous diazocine systems. Diazocines are bridged azobenzenes.[21] Imposed by the ring strain of the central eight-membered ring, the *cis* configuration (boat conformation) is more stable than the *trans* isomer (twist conformation). Upon irradiation with ~400 nm the *cis* form switches to the *trans* isomer, and irradiation with ~500 nm or heating leads back to the *cis* form.[22] Hence, the diazocines are quasi reversed azobenzenes that are more stable in their *trans* configurations.[23]

To investigate the electronic coupling effects, we synthesized two diazocine derivatized TATA platforms with ethynyl spacers (diazocine-TATAs). In compound **1** the diazocine is connected to the platform with the ethynyl group in *para* position to the azo group, providing a full π conjugation path of the N=N unit through the ethynyl spacer into the platform. Diazocine-TATA **2** is connected in *meta* position and thus interrupting conjugation.[24,25] Both diazocine-TATAs are equipped with methoxy groups, which serve as “reporter units” indicating the configuration of the molecules on metal surfaces.[15] In **1** the OMe group is attached *para* and in **2** the methoxy group is *meta* with respect to the azo group. Model calculations predict that the C_{phenyl}-O bonds in the *cis* isomers thus are parallel, and in the *trans* isomers orthogonal to the surface (Figure 1). Previous investigations have shown that IRRAS (Infrared Absorption Reflection Spectroscopy) in combination with the surface selection rules (stretching mode orthogonal to the surface→high intensity, parallel to the surface→low intensity) is a suitable method to determine the configuration and to measure kinetics on surfaces.[15] The C-O stretching frequencies proved to be ideal reporter signas to determine the configuration and to measure kinetics in monolayers of Azo-TATAs on surfaces.

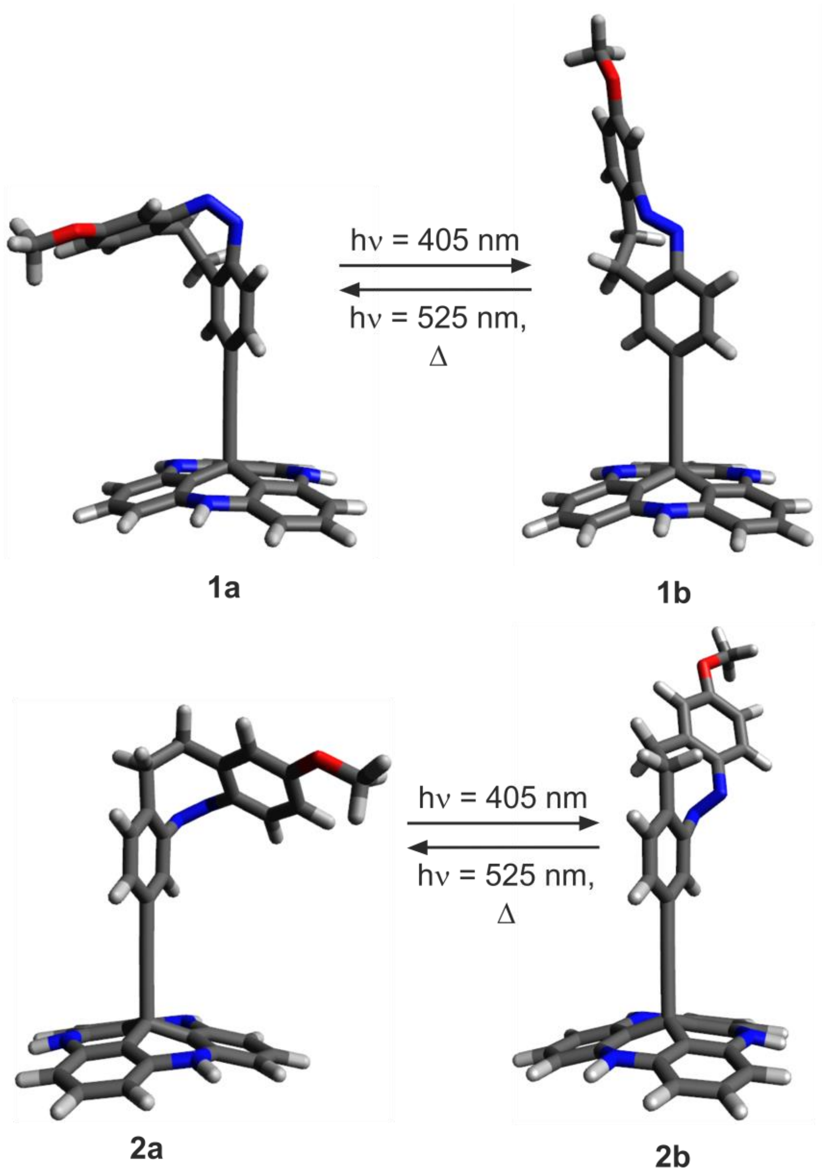


Figure 1: Structures of diazocine platform molecules (diazocine-TATAs) **1** and **2** in *cis* (**1a**, **2a**) and *trans* configuration (**1b**, **2b**) (octyl side chains are replaced to protons for simplification). The *cis*-diazocines (**1a**, **2a**) isomerize with 405 nm to the metastable *trans* diazocines (**1b**, **2b**) and with 530 nm or thermally back to the *cis* diazocines (**1a**, **2a**).

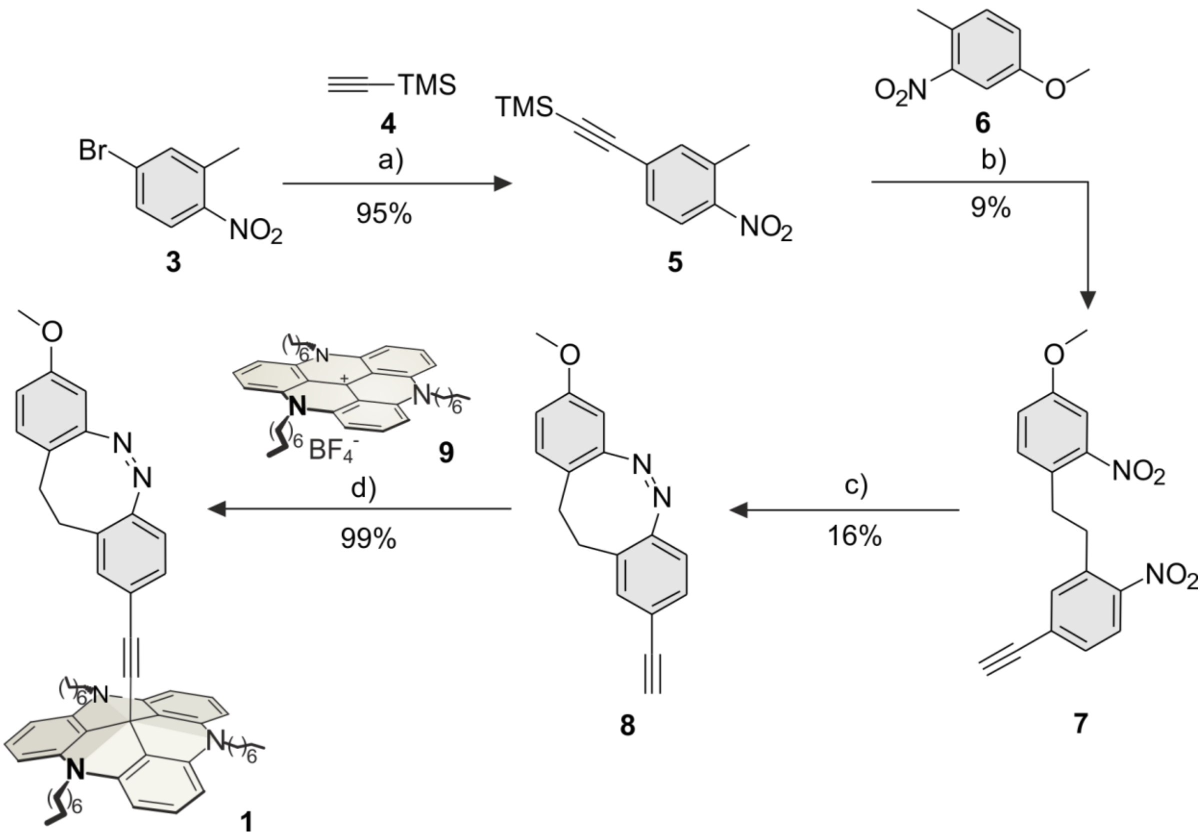
Results and Discussion

To obtain information on preferred conformations of **1** and **2** in their *cis* and *trans* configurations and to predict thermodynamic and kinetic stabilities, we performed DFT calculations at the M06-2X/def2-TZVP level of theory (for details see Supporting Information VI). As expected for diazocine based molecules our calculations predict the *cis* configuration for both compounds as the thermodynamically most stable isomer. For the corresponding *trans* configuration two different conformations were found: the twist and the chair structures. The twist conformation is about 2.5 kcal mol^{-1} more stable than chair. Our calculations predict reaction barriers (*trans*-twist→*cis*-boat) for both compounds of approximately 23 kcal mol^{-1} (96 kJ mol^{-1}). Obviously, the TATA platform and the ethinyl spacer have only marginal effect on the isomerization process. Hence, the diazocines **1** and **2** are ideal candidates to investigate the effect of bulk gold as a function of electronic coupling (conjugation) of the azo unit to gold.

Table 1: Quantum chemical calculated energies E_{rel} (M06-2X/def2-TZVP) of the twist and chair conformation of the *trans* configuration of *para* ethinyl substituted diazocine **1b** (*para* diazocine), and *meta* diazocine **2b**, relative to the boat conformation of the *cis* isomers **1a** and **2a**. $\Delta H^{\neq}$ are the calculated reaction barriers (*trans*-twist→*cis*-boat). All energies are given in kcal mol^{-1}.

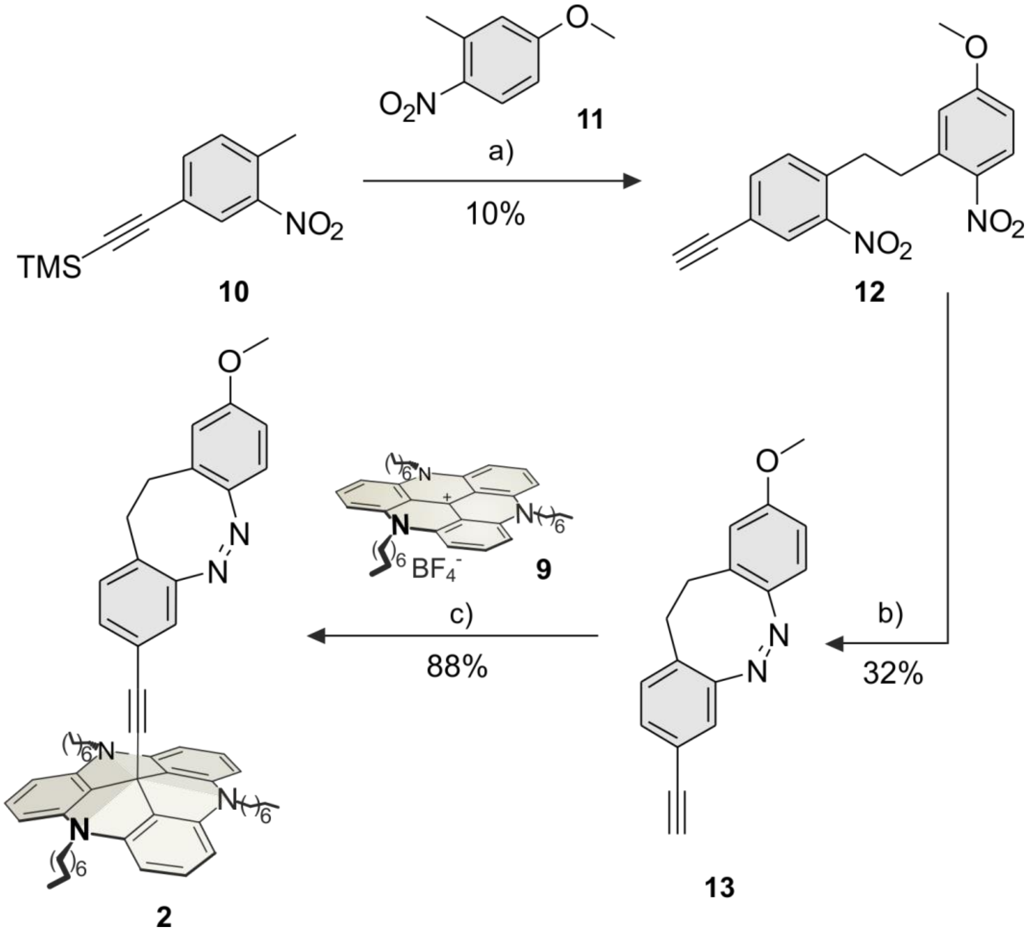
	E_{rel} *trans* twist	E_{rel} *trans* chair	$\Delta H^{\neq}$
para diazocine **1**	7.9	10.6	22.6
meta diazocine **2**	8.0	10.3	23.0

The *para* diazocine-TATA **1** was synthesized in a 5 step synthesis route (Scheme 1). Bromo toluene **3** was synthesized as described.[26] In a SONOGASHIRA cross coupling reaction acetylene substituted toluene **5** was achieved from bromo toluene **3** with TMS protected acetylene **4** (99%). The C-C bond formation of **5** and **6** to give dibenzoyl **7** was achieved with potassium butoxide and elemental bromine (9%) according to a literature procedure.[27] The *p*-ethynyl-diazocine **8** was obtained by reduction of both nitro groups, followed by oxidation of the formed hydrazine (16%). The unprotected ethynyl diazocine **8** was deprotonated with potassium hydroxide and functionalized at the central carbon atom of TATA platform **9** (synthesized according to LAURSEN and KREBS[28]) to obtain target *para* diazocine mounted on octyl substituted TATA platform **1** (99%).



Scheme 1: Synthesis route of *para*-diazocine platform molecule **1**. a) Pd(dppf)Cl_2, Cu(I)I, Et_3N, 3 h, 75 °C; b) 1: KO*t*Bu, THF, 2 min, -4 °C, N_2; 2: Br_2, 3.5 min, -4 °C; c) 1: $Ba(OH)_2$, Zn, EtOH, H_2O, 3.5 h, rt; 2: 0.1 M NaOH/MeOH, Cu(II)Cl_2, 15 h, rt; d) KOH, THF, 3.5 h, reflux, N_2.

The synthesis of the *meta* diazocine platform molecule **2** was achieved in a 4 step synthesis route (Scheme 2). Nitrotoluene **10** was synthesized as described in literature.[29] The formation of ethynyl toluene **10** and methoxy toluene **11** gave dibenzoyl **12** (10%) according to the same procedure as for dibenzoyl **7** (Scheme 1). Diazocine **13** was obtained by reduction and oxidation in moderate yields (32%). The reaction of diazocine **13** with the TATA ion **9** gave the target diazocine **1** (88%).



Scheme 2: Synthesis route of *meta*-diazocine platform **2**. a) 1: KO*t*Bu, THF, 2 min, -4 °C, N_2; 2: Br_2, 3.5 min, -4 °C, N_2; b) 1: $Ba(OH)_2$, Zn, EtOH, H_2O, 3.5 h, rt; 2: 0.1 M NaOH/MeOH, $Cu(II)Cl_2$, 15 h, rt; c) KOH, THF, 2 h, reflux, N_2.

The photophysical properties and the switching behaviour of **1** and **2** were determined in solution (THF). The UV-Vis spectra of **1** and **2** are shown before and after irradiation with 405 nm and 530 nm. Both diazocine-TATAs **1** and **2** exhibit similar UV spectra. The $n\pi^*$ transition of *cis*-**1** appears at 403 nm and at 494 nm in the *trans* isomer. The corresponding absorption maxima in diazocine-TATA **2** are 409 nm and 493 nm (Figure 2).

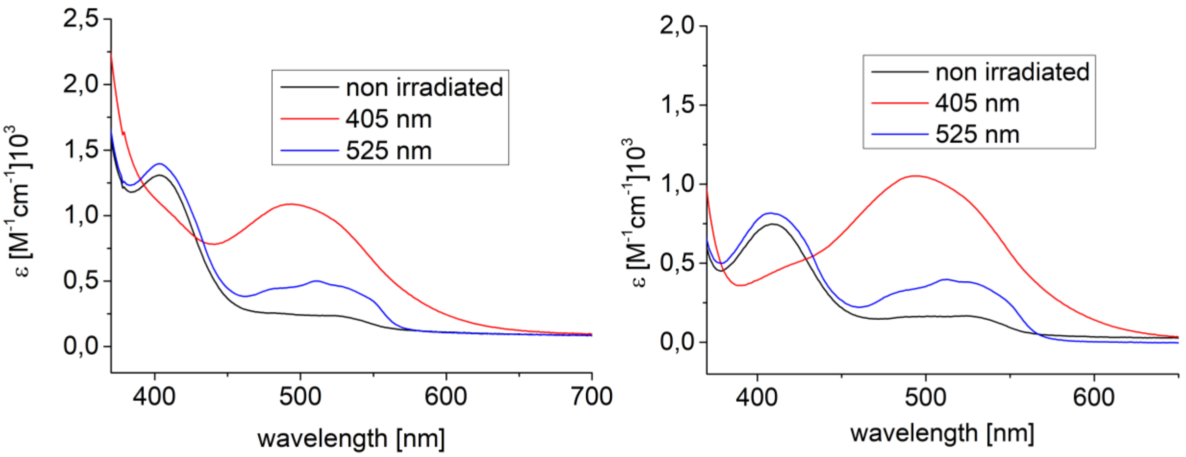


Figure 2: UV-Vis spectra of **1** (left) and **2** (right) in THF at room temperature. Black: as synthesized, red: after irradiation with 405 nm, and blue: after irradiation with 530 nm.

The photostationary states of **1** and **2** were determined in toluene-d_8 by ^{1}H NMR measurements (Table 2). Optimal wavelengths for the *cis*→*trans* isomerization are 405 nm (**1**: 53%, **2**: 65% *trans*). Back-isomerization to the *cis* isomer with 530 nm is nearly quantitative. The half-lives (298 K) are similar for both systems (2.12 h for **1** and 2.32 h for **2**). The lack of conjugation between azo function and ethynyl spacer of **2** yields in a slightly higher half-life which is in agreement with earlier results.[11]

Table 2: Photo stationary states (PSS) of *para* diazocine-TATA **1** (2.05 mmol/L) and *meta* diazocine-TATA **2** (2.27 mmol/L) upon irradiation with light of 405 nm, 530 nm and thermal isomerization half-life ($t_{1/2}$) determined with ^{1}H NMR spectroscopy (in deuterated toluene). The activation energies (E_a) are calculated from the linear fit of an Arrhenius plot.

	para diazocine **1**	*meta* diazocine **2**
PSS (405 nm)	53% (*trans*)	65% (*trans*)
PSS (530 nm)	93% (*cis*)	93% (*cis*)
$t_{1/2}$ (290.5 K)	5.27 h	5.76 h
$t_{1/2}$ (298 K)	2.12 h	2.32 h
$t_{1/2}$ (308 K)	0.69 h	0.73 h
E_A (kJ mol^{-1})	86.5	84.7

STM Measurements

The adsorption behavior of the diazocine-TATA molecules on Au(111) surfaces was studied by STM at room temperature (Figure 3). Adlayers of both compounds show a hexagonally ordered superstructure with lattice constants of **1** and **2** being (12.2 ± 0.6) Å and (12.1 ± 0.5) Å, respectively. Additionally, two rotational domains with an angle of (15 ± 4)° are observed. Altogether these parameters are in good agreement with a (√19 x √19) *R*23.4° superstructure which has been also observed in previous STM investigations of TATA and azobenzene-TATA molecules with octyl ligands.[30-32]

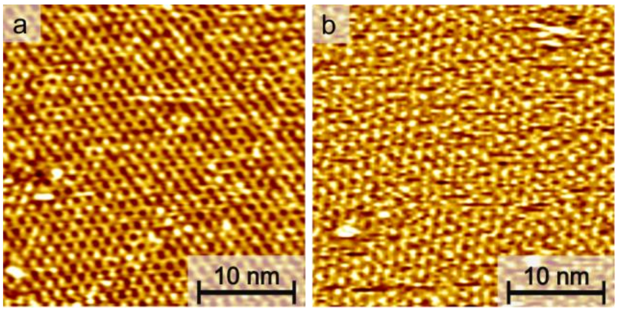


Figure 3: STM images (30 x 30 nm², U_{bias} = 0.3 V, I_t = 40 pA) of self-assembled monolayers of (a) compound **1** and (b) compound **2** on Au(111).

Conclusion

In summary, we present the syntheses of two different diazocines mounted on TATA platforms (**1-2**). The photochemical switching between the stable *cis* and metastable *trans* isomers was investigated. Upon irradiation with light of 405 nm diazocine-TATAs **1** and **2** convert to their *trans* configurations in moderate to good yields. The metastable *trans* isomers of **1** and **2** isomerize back to the *cis* isomer with half-lives of 2.12 h and 2.32 h at 298 K. The *trans→cis* activation energies with 86.5 kJ mol^{-1} for **1** and with 84.7 kJ mol^{-1} for **2** are similar to the structurally related azobenzenes.[11] Both diazocines form highly ordered monolayers on Au(111) surfaces. Further studies will include IRRAS measurements to determine the *trans→cis* isomerization kinetics on Au(111) surfaces.

Experimental

For detailed experimental procedures, including NMR, UV/vis and MS spectra see Supporting Information I-IV, for kinetic studies see Supporting Information V.

General Experimental Methods. All compounds were characterized using ^{1}H and ^{13}C NMR spectroscopy. The signals were assigned using 2D spectroscopy. For ^{1}H and ^{13}C NMR assignment we performed HSQC and HMBC. NMR spectra were measured in deuterated solvents (Deutero). Analytic measurements were performed by the following instruments: Bruker CABAV 500neo (^{1}H NMR: 500 MHz, ^{13}C NMR: 125 MHz, ^{29}Si NMR: 99 MHz) and Bruker AV 600 (^{1}H NMR: 600 MHz, ^{13}C NMR: 150 MHz). Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrometer with an A531-G Golden-Gate-Diamon-ATR-unit. The high-resolution (HR) mass spectra were measured with an APEX 3 FT-ICR with a 7.05 T magnet by co. Bruker Daltonics. Electron impact (EI). Matrix-assisted Laser Desorption/Ionization (MALDI) mass spectra were measured with a Bruker MALDI-TOF Autoflex.

1-Methyl-2-nitro-5-(2-(trimethylsilyl)ethynyl)-benzene (5). In triethylamine (dry, 80 mL) 4-bromo-2-methyl-1-nitrobenzol[26] **3** (6.00 g, 27.8 mmol), trimethylsilyl-acetylene (5.21 mL, 36.1 mmol), Pd(dppf)Cl_2 (1.02 g, 1.39 mmol, 5%) and copper(I)iodide (530 mg, 2.78 mmol, 10%) were suspended under nitrogen atmosphere and stirred for 1 h at 60 °C. The reaction solution was filtered over celite and the solvent was removed under reduced pressure. The crude product was purified via column chromatography (silica gel, dichloromethane) to obtain a grey solid (6.14 g, 26.3 mmol, 95%). **^{1}H NMR** (500.1 MHz, $CDCl_3$, 298 K, TMS): δ = 7.93 (d, ^3J = 8.4 Hz, 1H, *H*-3), 7.43 (s, 1H, *H*-6), 7.40 (dd, ^3J = 8.5 Hz, ^4J = 1.6 Hz, 1H, *H*-4), 2.58 (s, 3H, *H*-10), 0.27 (s, 9H, *H*-9) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K, CH_3Cl): δ = 148.43 (s, *C*-2), 136.21 (s, *C*-6), 133.98 (s, *C*-1), 130.30 (s, *C*-4), 128.47 (s, *C*-5), 124.93 (s, *C*-3), 102.91 (s, *C*-7), 99.44 (s, *C*-8), 20.53 (s, *C*-10), -0.12 (s, *C*-9) ppm. **^{29}Si NMR** (99.4 MHz, $CDCl_3$, 298 K): δ = -16.99 ppm. **MS** (EI, 70eV): m/z = 233.09 $[M]^+$. **IR** (ATR): $\tilde{v}$ = 2957 (w), 2159 (w), 1601 (w), 1578 (w), 1515 (s), 1479 (w), 1348 (s), 1244 (s), 949 (m), 834 (vs), 756 (s), 698 (m), 663 (s), 450 (m) cm^{-1}. **m.p.** = 76.5 °C. **HRMS** (EI, 70 eV): m/z $[M]^+$ calcd. for $C_{12}H_{15}NO_2Si$: 233.08720; found: 233.08700.

Trimethyl((4-nitro-3-(4-methoxy-2-nitrophenylethyl)phenyl)acetylene (7). In tetrahydrofurane (abs., 250 mL) 1-methyl-2-nitro-5-(2-(trimethylsilyl)ethynyl)-benzene **5** (5.00 g, 21.4 mmol) and 4-methoxy-1-methyl-2-nitrobenzene **6** (2.97 ml, 21.4 mmol) were dissolved under nitrogen atmosphere and the solution was cooled to 0 °C. Potassium butoxide (3.40 g, 27.8 mmol) was added and stirred for 3 min before addition of bromine (1.42 mL, 27.8 mmol). After stirring for 5 min, the reaction was poured onto ice/water (500 mL). The solution was extracted with dichloromethane (3x 300 mL) and the combined organic layers were washed with saturated sodium thiosulfate solution and saturated sodium chloride solution and then dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified via column chromatography (silica gel, cyclohexane/ethyl acetate, 2/1) to obtain a beige solid (615 mg, 1.89 mmol, 9%). **^{1}H NMR** (500.1 MHz, $CDCl_3$, 298 K, TMS): δ = 7.92 (d, ^{3}J = 8.5 Hz, 1H, *H*-11), 7.55 (d, ^{4}J = 1.8 Hz, 1H, *H*-14), 7.50 (d, ^{4}J = 2.7 Hz, 1H, *H*-3), 7.47 (dd, ^{3}J = 8.4 Hz, ^{4}J = 1.8 Hz, 1H, *H*-12), 7.31 (d, ^{3}J = 8.5 Hz, 1H, *H*-6), 7.11 (dd, ^{3}J = 8.5 Hz, ^{4}J = 2.7 Hz, 1H, *H*-5), 3.87 (s, 3H, *H*-15), 3.30 (s, 1H, *H*-17), 3.23-3.13 (m, 4H, *H*-7, *H*-8) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 300 K, TMS): δ = 158.61 (s, *C*-4), 149.43 (s, *C*-2), 148.63 (s, *C*-10), 136.49 (s, *C*-9), 136.01 (s, *C*-14), 133.27 (s, *C*-6), 130.94 (s, *C*-12), 127.76 (s, *C*-1), 127.59 (s, *C*-13), 124.98 (s, *C*-11), 120.28 (s, *C*-5), 109.35 (s, *C*-3), 81.55 (s, *C*-17), 55.85 (s, *C*-15), 34.36 (s, *C*-8), 33.79 (s, *C*-7) ppm. **MS** (EI, 70eV): m/z = 326.08 $[M]^{+}$. **IR** (ATR): $\tilde{\nu}$ = 3286 (m), 2939 (br. w), 1602 (s), 1573 (w), 1485 (vs), 1461 (m), 1309 (w), 1278 (s), 1245 (vs), 1156 (w), 1107 (w), 1037 (m), 898 (w), 865 (w), 812 (m), 658 (w), 616 (w) cm^{-1}. **m.p.** = 104.1 °C. **HRMS** (EI, 70 eV): m/z $[M]^{+}$ calcd. for $C_{17}H_{14}N_2O_5$: 326.09027; found: 326.09052.

(Z)-4-Ethynyl-9-methoxy-11,12-dihydrodibenzo(c,g)(1,2)-diazocine (8). In ethanol (100 mL) trimethyl(4-nitro-3-(4-methoxy-2-nitrophenylethyl)phenyl)acetylene **7** (400 mg, 1.23 mmol) was dissolved, an aqueous solution of barium hydroxide $[Ba(OH)_2 \cdot 8H_2O]$ (1.16 g, 3.68 mmol) in H_2O (40 mL) and zinc powder (1.29 g, 19.7 mmol) were added. The reaction was refluxed for 4.75 h. The reaction mixture was filtered through celite and the solvent was removed under reduced pressure. The crude product was dissolved in dichloromethane, filtered through celite and the solvent was removed under reduced pressure. The crude product was dissolved in 0.1 M methanolic NaOH solution (120 mL), $CuCl_2$ (6.60 mg, 49.1 µmol) was added and air was bubbled through the solution for 6 h at room temperature. The reaction was neutralized with 1 M hydrogen chloride solution and saturated sodium bicarbonate solution (150 mL) was added. The aqueous layer was extracted with dichloromethane (3x 150 mL) and the solvent was removed under reduced pressure. The crude product was purified via column chromatography (silica gel, cyclohexane/ethyl acetate, 2/1) to obtain an orange solid (51.0 mg, 194 µmol, 16%).

^{1}H NMR (500.1 MHz, acetone-d$_6$, 298 K, TMS): δ = 7.28 (dd, ^3J = 8.1 Hz, ^4J = 1.7 Hz, 1H, *H*-12), 7.20 (d, ^4J = 1.6 Hz, 1H, *H*-14), 6.97 (d, ^3J = 8.4 Hz, 1H, *H*-6), 6.83 (d, ^3J = 8.1 Hz, 1H, *H*-11), 6.61 (dd, ^3J = 8.4 Hz, ^4J = 2.6 Hz, 1H, *H*-5), 6.39 (d, ^4J = 2.7 Hz, 1H, *H*-3), 3.71 (s, 3H, *H*-15), 3.59 (s, 1H, *H*-17), 2.87-2.81 (m, 4H, *H*-7, *H*-8) ppm. **^{13}C NMR** (125.8 MHz, acetone-d$_6$, 298 K, acetone): δ = 159.44 (s, *C*-4), 157.41 (s, *C*-2), 156.85 (s, *C*-10), 134.12 (s, *C*-14), 131.82 (s, *C*-6), 131.10 (s, *C*-12), 130.21 (s, *C*-9), 121.72 (s, *C*-13), 120.61 (s, *C*-1), 119.68 (s, *C*-11), 113.61 (s, *C*-5), 104.60 (s, *C*-3), 83.52 (s, *C*-16), 79.25 (s, *C*-17), 55.66 (s, *C*-15), 31.86 (s, *C*-8), 31.10 (s, *C*-7) ppm. **MS** (EI, 70eV): m/z = 262.11 $[M]^+$. **IR** (ATR)**:** ṽ = 3275 (m), 1605 (w), 1493 (s), 1393 (w), 1251 (m), 1143 (w), 1065 (w), 1030 (vs), 999 (s), 899 (w), 811 (vs), 671 (s), 616 (s), 509 (s) cm^{-1}. **m.p.** = 133.8 °C. **HRMS** (EI, 70 eV): m/z $[M]^+$ calcd. for $C_{17}H_{14}N_2O$: 262.11061; found: 262.11019.

(Z)-12c-(4-Ethynyl-9-methoxy-11,12-dihydrodibenzo(c,g)(1,2)diazocin-10-yl)ethynyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene (1) In tetrahydrofurane (abs., 30 mL) (Z)-4-ethynyl-9-methoxy-11,12-dihydrodibenzo(c,g)(1,2)-diazocine **8** (46.0 mg, 175 µmol), octyl-TATA-BF$_4$[28] **9** (161 mg, 228 µmol) and powdered potassium hydroxide (105 mg, 1.87 mmol) were suspended under nitrogen atmosphere and refluxed for 3.5 h. The reaction was poured onto saturated sodium chloride solution (20 mL) and the aqueous layer was extracted with diethyl ether (3x 30 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified via column chromatography (aluminium oxide, basic, diethylether) to obtain an orange solid (153 mg, 174 µmol, 99%). **^{1}H NMR** (500.1 MHz, acetone-d$_6$, 298 K, TMS): δ = 7.18 (t, ^3J = 8.3 Hz, 3H, *H*-22), 6.85-6.80 (m, 2H, *H*-6, *H*-12), 6.72 (d, ^4J = 1.6 Hz, 1H, *H*-14), 6.65-6.60 (m, 7H, *H*-11, *H*-21), 6.47 (dd, ^3J = 8.4 Hz, ^4J = 2.7 Hz, 1H, *H*-5), 6.26 (d, ^4J = 2.6 Hz, 1H, *H*-3), 3.99-3.93 (ps. t, 6H, *H*-23), 3.63 (s, 3H, *H*-15), 2.76-2.62 (m, 4H, *H*-7, *H*-8), 1.84-1.77 (ps. sechst., 6H, *H*-24), 1.52-1.45 (ps. pent., 6H, *H*-25), 1.41-1.21 (m, 24H, *H*-26, *H*-27, *H*-28, *H*-29), 0.90-0.85 (ps. t, 9H, *H*-30) ppm. **^{13}C NMR** (125.8 MHz, acetone-d$_6$, 298 K, acetone): δ = 159.31 (s, *C*-4), 157.40 (s, *C*-2), 156.04 (s, *C*-10), 141.34 (s, *C*-20), 133.14 (s, *C*-14), 131.61 (s, *C*-6), 130.32 (s, *C*-12), 129.81 (s, *C*-9), 129.38 (s, *C*-22), 123.01 (s, *C*-13), 120.62 (s, *C*-1), 119.25 (s, *C*-11), 113.28 (s, *C*-5), 110.82 (s, *C*-19), 106.03 (s, *C*-21), 104.50 (s, *C*-3), 94.77 (s, *C*-17), 83.72 (s, *C*-16), 55.56 (s, *C*-15), 46.72 (s, *C*-23), 32.58 (s, *C*-29), 31.77 (s, *C*-8), 31.01 (s, *C*-7), 30.11 (s, C-26), 30.06 (s, C-27), 27.43 (s, *C*-25), 26.62 (s, *C*-24), 23.33 (s, *C*-28), 14.40 (s, *C*-30) ppm. **MS** (MALDI-TOF, Cl-CCA): m/z = 879.6 $[M]^+$. **IR** (ATR)**:** $\tilde{v}$ = 2924 (m), 2852 (m), 1614 (vs), 1579 (vs), 1482 (vs), 1457 (vs), 1393 (vs), 1267 (m), 1242 (s), 1167 (s), 1145 (m), 1036 (w), 895 (w), 809 (w), 772 (m), 748 (m), 726 (s), 657 (w) cm^{-1}.

Trimethyl((3-nitro-4-(5-methoxy-2-nitrophenylethyl)phenyl)acetylene (12). In tetrahydrofurane (abs., 280 mL) 1-methyl-2-nitro-4-(2-(trimethylsilyl)ethynyl)-benzene[29] **10** (6.00 g, 25.7 mmol) and 4-methoxy-2-methyl-1-nitrobenzene **11** (6.45 g, 30.9 mmol) were dissolved under nitrogen atmosphere and cooled to 0 °C. Potassium butoxide (4.40 g, 36.0 mmol) was added and stirred for 3 min before addition of bromine (1.84 mL, 36.0 mmol). After stirring for 5 min, the reaction was poured onto ice/water (500 mL). The solution was extracted with dichloromethane (3x 300 mL) and the combined organic layers were washed with saturated sodium thiosulfate solution and saturated sodium chloride solution and then dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified via column chromatography (silica gel, cyclohexane/ethyl acetate, 2/1) to obtain a beige solid (817 mg, 2.50 mmol, 10%). **^{1}H NMR** (600.1 MHz, $CDCl_3$, 298 K, TMS): δ = 8.10 (d, ^3J = 9.0 Hz, 1H, *H*-3), 8.06 (d, ^4J = 1.6 Hz, 1H, *H*-11), 7.63 (dd, ^3J = 8.0 Hz, 1H, *H*-13), 7.44 (d, ^3J = 7.9 Hz, 1H, *H*-14), 6.85 (dd, ^3J = 9.1 Hz, ^4J = 2.8 Hz, 1H, *H*-4), 6.83 (d, ^4J = 2.8 Hz, 1H, *H*-6), 3.88 (s, 3H, *H*-15), 3.30-3.21 (m, 4H, *H*-7, *H*-8), 3.18 (s, 1H, *H*-17) ppm. **^{13}C NMR** (150.9 MHz, $CDCl_3$, 298 K, TMS): δ = 163.40 (s, *C*-5), 149.01 (s, *C*-10), 141.85 (s, *C*-2), 139.20 (s, *C*-1), 136.67 (s, *C*-9), 136.38 (s, *C*-13), 132.67 (s, *C*-14), 128.24 (s, *C*-11), 127.97 (s, *C*-3), 121.96 (s, *C*-12), 116.85 (s, *C*-4), 112.97 (s, *C*-6), 81.00 (s, *C*-16), 79.56 (s, *C*-17), 55.89 (s, *C*-15), 35.37 (s, *C*-7), 34.14 (s, *C*-8) ppm. **MS** (EI, 70eV): m/z = 326.01 $[M]^+$. **IR** (ATR): $\tilde{v}$ = 3274 (m), 1601 (m), 1586 (m), 1548 (w), 1521 (s), 1500 (s), 1455 (w), 1343 (m), 1327 (vs), 1298 (w), 1258 (vs), 1211 (m), 1077 /m), 1069 (m), 1030 (m), 896 (m), 870 (m), 831 (m), 804 (m), 762 (m), 699 (m) cm^{-1}. **m.p.** = 127.1 °C. **HRMS** (EI, 70 eV): m/z $[M]^+$ calcd. for $C_{17}H_{14}N_2O_5$: 326.09027; found: 326.09068.

(Z)-3-Ethynyl-10-methoxy-11,12-dihydrodibenzo(c,g)(1,2)-diazocine (13). In ethanol (80 mL) trimethyl(3-nitro-4-(5-methoxy-2-nitrophenylethyl)phenyl)acetylene **12** (396 mg, 1.21 mmol) was dissolved, an aqueous solution of barium hydroxide $[Ba(OH)_2 \cdot 8H_2O]$ (1.15 g, 3.64 mmol) in H_2O (34 mL) and zinc powder (1.27 g, 19.4 mmol) were added. The reaction was refluxed for 4.75 h. The reaction mixture was filtered through celite and the solvent was removed under reduced pressure. The crude product was dissolved in dichloromethane (50 mL), filtered through celite and the solvent was removed under reduced pressure. The crude product was dissolved in 0.1 M sodium hydroxide solution in methanol (120 mL), $CuCl_2$ (6.5 mg, 48 µmol) was added and air was bubbled through the solution for 13 h at room temperature. The reaction was neutralized with 1 M hydrogen chloride solution and saturated sodium bicarbonate solution (200 mL) was added. The aqueous layer was extracted with dichloromethane and the solvent was removed under reduced pressure. The crude product was purified via column chromatography (silica gel, cyclohexane/ethyl acetate, 2/1) to obtain an orange solid (69.0 mg, 263 µmol, 22%). **^{1}H NMR** (500.1 MHz, $CDCl_3$, 298 K, TMS): δ = 7.15 (dd, ^3J = 7.9 Hz, ^4J = 1.6 Hz, 1H, *H*-13), 6.96 (d, ^3J = 7.8 Hz, 1H, *H*-14), 6.94 (d, ^4J = 1.6 Hz, 1H, *H*-11), 6.83 (d, ^3J = 8.7 Hz, 1H, *H*-3), 6.69 (dd, ^3J = 8.6 Hz, ^4J = 2.6 Hz, 1H, *H*-4), 6.49 (d, ^4J = 2.6 Hz, 1H, *H*-6), 3.71 (s, 3H, *H*-15), 3.03 (s, 1H, *H*-17), 2.85 (m, 4H, *H*-7, *H*-8) ppm. **^{13}C NMR** (125.8 MHz, $CDCl_3$, 298 K, TMS): δ = 158.36 (s, *C*-5), 155.27 (s, *C*-10), 148.95 (s, *C*-2), 130.61 (s, *C*-13), 129.64 (s, *C*-14), 129.46 (s, *C*-9), 129.15 (s, *C*-1), 122.37 (s, *C*-11), 120.94 (s, *C*-3), 120.54 (s, *C*-12), 114.77 (s, *C*-6), 111.98 (s, *C*-4), 82.71 (s, *C*-16), 77.62 (s, C-17), 55.27 (s, *C*-15), 32.08 (s, *C*-7), 31.47 (s, *C*-8) ppm. **MS** (EI, 70eV): m/z = 262.11 $[M]^+$. **IR** (ATR): $\tilde{v}$ = 3265 (m), 2919 (br. w), 2851 (w), 1609 (w), 1575 (m), 1483 (s), 1464 (m), 1427 (m), 1308 (m), 1259 (vs), 1154 (m), 1110 (m), 1040 (m), 864 (m), 819 (m), 798 (vs), 703 (m), 613 (s), 586 (s) cm^{-1}. **m.p.** = 112.1 °C. **HRMS** (EI, 70 eV): m/z $[M]^+$ calcd. for $C_{17}H_{14}N_2O$: 262.11061; found: 262.11016.

(Z)-12c-(3-Ethynyl-10-methoxy-11,12-dihydrodibenzo(c,g)(1,2)diazocin-10-yl)ethynyl-4,8,12-tri-*n*-octyl-4,8,12-triazatriangulene (2). In tetrahydrofurane (abs., 10 mL) (Z)-3-ethynyl-10-methoxy-11,12-dihydrodibenzo(c,g)(1,2)-diazocine **13** (20.0 mg, 76.2 µmol), octyl-TATA-BF_4[28] **9** (64.6 mg, 91.5 µmol) and powdered potassium hydroxide (34.2 mg, 610 µmol) were suspended under nitrogen atmosphere and refluxed for 2 h. The reaction was poured onto saturated sodium chloride solution (30 mL) and extracted with diethyl ether (3x 25 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified via column chromatography (aluminium oxide, basic, diethylether) to obtain an orange solid (59.0 mg, 67.0 µmol, 88%). **^{1}H NMR** (500.1 MHz, acetone-d_6, 298 K, TMS): δ = 7.18 (t, ^3J = 8.24 Hz, 3H, *H*-22), 6.89 (d, ^3J = 8.0 Hz, 1H, *H*-9), 6.71 (dd, ^3J = 8.0 Hz, ^4J= 1.7 Hz, 1H, *H*-14), 6.68 (d, ^3J = 8.5 Hz, 1H, *H*-3), 6.65-6.60 (m, 7H, *H*-4, *H*-21), 6.52 (d, ^4J = 2.6 Hz, 1H, *H*-6), 6.44 (d, ^4J = 1.6 Hz, 1H, *H*-12), 3.99-3.93 (ps. t, 6H, *H*-23), 3.63 (s, 3H, *H*-15), 2.78-2.69 (m, 4H, *H*-7, *H*-8), 1.85-1.76 (ps. pent., 6H, *H*-24), 1.52-1.44 (ps. pent., 6H, *H*-25), 1.41-1.22 (m, 24H, *H*-26, *H*-27, *H*-28, *H*-29), 0.90-0.85 (ps. t, 9H, *H*-30) ppm. **^{13}C NMR** (125.8 MHz, acetone-d_6, 298 K, acetone): δ = 159.25 (s, *C*-5), 156.54 (s, *C*-11), 150.00 (s, *C*-2), 141.36 (s, *C*-20), 130.52 (s, *C*-9), 130.38 (s, *C*-14), 130.27 (s, *C*-1), 129.44 (s, *C*-10), 129.38 (s, *C*-22), 122.89 (s, *C*-13), 121.52 (s, *C*-12), 121.15 (s, *C*-3), 115.65 (s, *C*-6), 112.54 (s, *C*-4), 110.86 (s, *C*-19), 106.05 (s, *C*-21), 95.09 (s, *C*-17), 83.45 (s, *C*-16), 55.48 (s, *C*-15), 46.67 (s, *C*-23), 32.57 (s, *C*-29), 32.38 (s, *C*-7), 31.73 (s, *C*-8), 30.10 (s, *C*-26), 30.05 (s, *C*-27), 27.43 (s, *C*-25), 26.65 (s, *C*-24), 23.32 (s, *C*-28), 14.40 (s, *C*-30) ppm. **MS** (MALDI-TOF): m/z = 879.6 $[M]^+$. **IR** (ATR): $\tilde{v}$ = 2924 (s), 2852 (m), 1614 (s), 1579 (vs), 1482 (vs), 1457 (vs), 1393 (vs), 1374 (m), 1243 (s), 1167 (s), 1039 (w), 911 (w), 807 (w), 772 (m), 750 (s), 724 (s), 657 (w) cm^{-1}.

STM. For the preparation of the self-assembled monolayers single-crystalline Au(111) substrates were flame annealed, immersed for 40 min. (compound **1**) and 4 hours (compound **2**) in 1-100 µM solutions of compound **1** or compound **2** in toluene or THF at temperatures between room temperature and 50 °C. Afterwards, the samples were rinsed with the pure solvent.

Supporting Information

The Supporting Information (Analytical methods, experimental procedures, NMR spectra, UV spectra, kinetic studies, DFT calculations) is available free of charge on the ACS Publications website at DOI:

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