A New Versatile Receptor Platform

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We prepared a molecular receptor based on the molecular tweezer concept. Our system offers versatility, an extremely short synthetic route, good yield, large quantities, and finally having binding constants that equal the best known tweezer molecules when it comes to binding various nitroaromatics such as 1,3,5-trinitrotoluene (24 M^{-1}), 1,3,5-trinitrobenzene (182 M^{-1}), and 2,4,7-trinitrofluorenone (490 M^{-1}) as determined using ^1H NMR in $CDCl_3$. It is notable that these binding constants are achieved although the molecular framework is not locked in a fixed and rigid conformation. The rigidity has been claimed to be the governing factor when it comes to achieving a large binding constant. We propose that our molecular tweezer system may be preorganized and that this explains the high binding constants observed. Further, we investigated the crystal structures of both the neutral receptor molecule and a complex with 1,3,5-trinitrobenzene and found that the molecule forms a pocket suited to accommodate flat aromatic analytes.

Introduction

During the past 30 years a considerable research effort has been placed toward obtaining receptor molecules specific for an analyte which typically is a small functional molecule such as a sugar, a neurotransmitter, a drug, explosives, etc. By and large most work has been centered around a family of molecules that have been used as the host molecule or receptor platform. The [*n*]cyclophanes[1−6] are an example of a popular molecular platform. Chemists have many reasons for their choice of molecular platform but largely the choice is determined by the ease at which the molecules can be synthesized. Normally the receptor molecule is much larger and has a higher level of molecular complexity than the analyte molecule for which it is specific. Since the platform molecule often has to be subjected to further synthetic elaboration to gain specificity it has to be available in pure form and in large quantities. Most platform molecules suffer in this respect, as they all have a lengthy synthetic path behind them before derivatives with various specificities are arrived at.

Molecular tweezers[7−28] are generally molecules that have two large aromatic plates connected by a hinge such that the interplanar distance between the two aromatic plates forms a pocket suitable for binding planar molecules. The concept has been known for a while,[7] and its applicability has been proven as a viable means of constructing a molecular receptor. Three schools have developed so far and have relied on rare[8−11] synthetic chemistry, on lengthy and tedious synthetic chemistry,[21] or on relatively simple synthetic chemistry based on naturally occurring starting materials with fixed stereochemistry but of low versatility.[15−17]

In this article we present a very versatile type of receptor platform. In essentially one synthetic step a large receptor molecule is made (Scheme 1).

A wide range of interactions with an analyte molecule are easily envisaged for instance specific hydrogen interactions, ionic interactions, and $\pi-\pi$ interactions.

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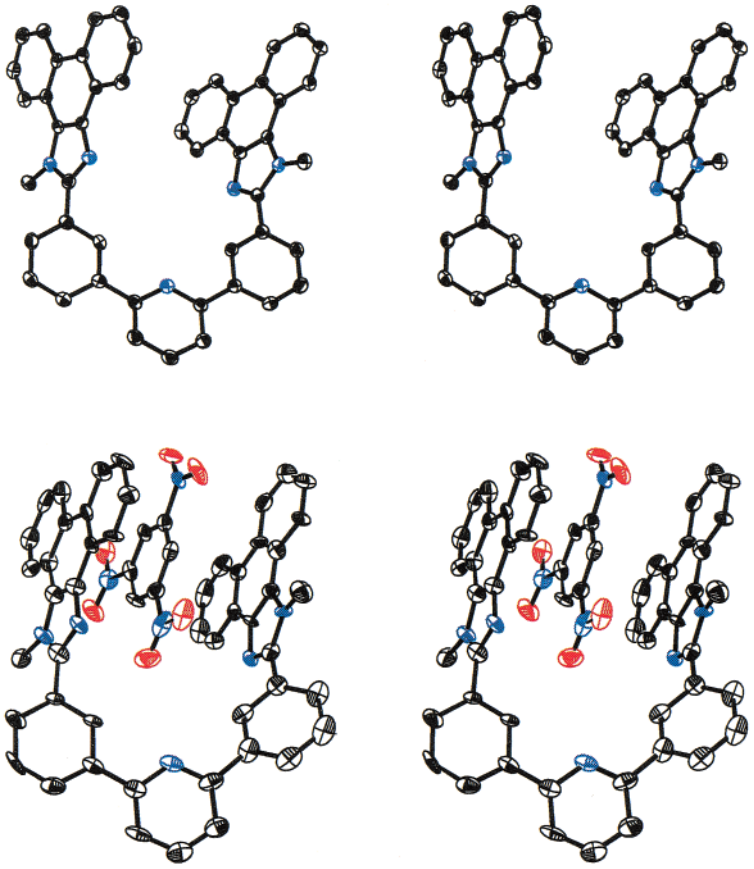
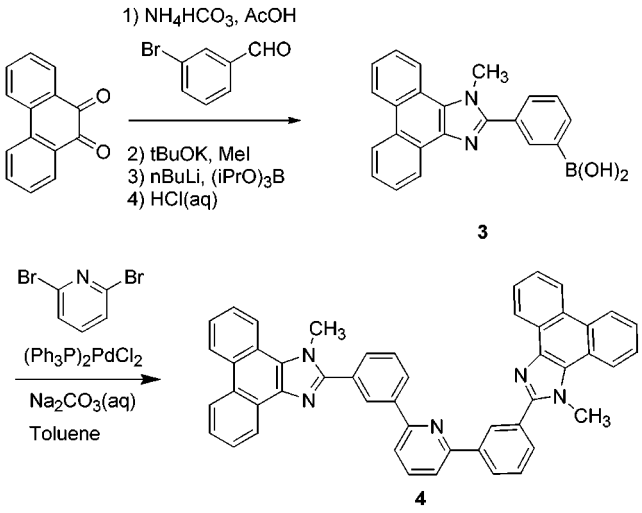


Figure 1. ORTEP stereo plots (50% ellipsoids) of the molecular geometry in the solid state as determined by X-ray crystallography. The neutral host (above) and the host with a 1,3,5-trinitrobenzene guest molecule (below, the solvent CH_2Cl_2 molecule has been omitted for clarity).

Scheme 1



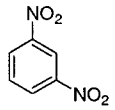
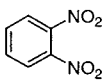
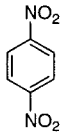
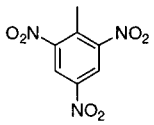
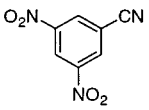
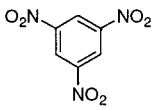
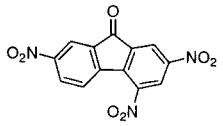
Results and Discussion

The Solid State. Our receptor molecule qualifies as a molecular tweezer and consists of two large aromatic plates separated at a distance sufficient to host a small planar molecule. The large plates are held in space by a linker or hinge region with few conformational degrees of freedom. In Figure 1 the molecular geometry in the solid state as determined by X-ray crystallography is shown for both the neutral molecule **4** as well as the geometry of 1:1 complex between **4** and 1,3,5-trinitrobenzene.

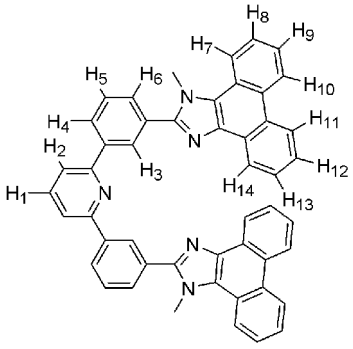
Slight changes in the thickness of the analyte can be accommodated by the twisting of the large plates with respect to the hinge. Only strongly electron deficient molecules bind well. For instance the neutral molecule **4** does not bind solvent dichlorobenzene when crystallizing. The average interplanar distance[29] was 6.8(4) Å (max/min = 7.672(3)/6.092(3) Å) between the 1-methylphenanthro[9,10-*d*]imidazol-2-yl groups which form an angle of 14.33(4)°. Further, the angle that these groups form with the hinge region are respectively for the two groups in the asymmetric unit 49.80(5)° and 55.75(5)°. In the crystal structure of the complex of **4** with 1,3,5-trinitrobenzene the interplanar average distance between the two 1-methyl-phenanthro[9,10-*d*]imidazol-2-yl groups is 6.48(13) Å (max/min = 6.66(1)/6.22(1) Å) which form angles of 3.76(6)° and 0.61(6)°, respectively. The two distances between the 1-methylphenanthro[9,10-*d*]imidazol-2-yl groups and the 1,3,5-trinitrobenzene guest molecule are 3.32(14) Å and 3.23(5) Å, respectively (max/min = 3.57(1)/3.05(1) Å and 3.47(1)/3.01(1) Å). The angles formed between the hinge region and the large aromatic plates is 42.65(24)° and 61.33(23)°, thus emphasising the conformational flexibility of this host system. Interestingly, the host molecule on its own seems to prefer having the aromatic plates in proximity; thus, one does not need to fix the geometry of the host to make it work as a

(29) In all instances the average interplanar distances were obtained by least-squares fitting the atoms of one of the planar group to a plane. The distances of the individual atoms of the other planar group was the worked out. Angles between planes were obtained by least-squares fitting the atoms of the individual planar groups to a plane. The angles between these two planes is then quoted.

Table 1. Binding Constants for the 1:1 Complex between Compound 4 and Various Analytes in $CDCl_3$ As Determined by NMR Titrations

Analyte							
K_{11}	< 1	< 1	6	24	55	182	490

Scheme 2



receptor. Both regions, the aromatic plates and the hinge, can in principle be tuned with respect to their interaction with the guest molecule. Comprehensive work by Zimmerman showed this to be of great importance.[20,21] The available interactions between the aromatic plates and the analyte are mainly $\pi-\pi$ interactions. Through appropriate synthetic elaboration π-donor or π-acceptor interactions can be envisaged. The interactions between the hinge region and the analyte that can be envisaged are specific hydrogen interactions (donor/none/acceptor) and acid/base interactions. As mentioned above, previous work on molecular tweezers generally relied on elaborate synthetic chemistry, making the synthesis of widely different receptors time-consuming, or relied on naturally occurring molecules, thus limiting the range of molecular structures that could be accessed with ease. With the strategy presented here, the facile synthesis of an array of receptor molecules with different specificities is possible. We have exemplified this type of system with a receptor molecule that binds electron deficient planar molecules in particular polynitroaromatics such as explosives.

In Solution. The ^1H spectrum of **4** can be subdivided into 11 independent spin systems as shown in Scheme 2. An A_2B (H1 and H2) system arising from the pyridine ring, two equivalent ABC (H4,H5,H6) systems from the adjoining benzene rings, equivalent singlets from the H3 protons, equivalent singlets from the *N*-methyl groups and two sets of equivalent AA′XX′ (H7,H8,H9,H10) (H11,H12,H13,H14). ^1H spectra were obtained in both $CDCl_3$ and DMSO-d_6, facilitating the assignment. The singlet at 4.28 ppm in $CDCl_3$ and 4.34 ppm in DMSO-d_6 clearly arises from the *N*-methyl groups. A singlet at 8.69 ppm in $CDCl_3$ and 8.75 ppm in DMSO is also straightforwardly assigned to the H3 protons. A COSY spectrum of the DMSO solution connects doublets at 8.52 and 7.97 ppm and a triplet at 7.79 in one spin system. Since the integrals of these three signals each corresponds to two protons, these signals must be assigned to the ABC system. The COSY spectrum of the DMSO solution also connects the two AA′XX′ systems. Two doublets at 8.93 and 8.48 ppm together with two distorted doublets at 8.82 and 8.60 ppm belongs to the A and A′ parts of these systems. The X and X′ signals are grouped together in a multiplet around 7.6 ppm. Finally, a multiplet centered around 8.1 ppm with the intensity of three protons can be assigned to the A_2B system.

A TOCSY spectrum was also obtained to confirm the assignments. Each spin system is clearly grouped together using this technique. The ABC system is seen to be connected through *meta* couplings to the singlet at 8.75 ppm assigned to the H3 protons. The spectrum in $CDCl_3$ solution is less well resolved since the XX′ parts have spread out over a larger range, obscuring a doublet of the ABC system and also overlapping the A_2B system.

Binding Studies. When molecules that bind well to the tweezer (i.e., 1,3,5-trinitrobenzene) are added to the solution, the ^1H spectrum changes dramatically due to shielding effects. It is notable that the signals arising from the protons in the 1-methylphenanthro[9,10-*d*]-imidazole-2-yl groups are moved to higher field while those in the bridge are moved to lower field. This is of course in agreement with the X-ray structure where the 1,3,5-trinitrobenzene molecule is placed in the cleft of the tweezer. Protons above and below the 1,3,5-trinitrobenzene plane are shielded (the plate protons) while protons in the TNB plane are deshielded (the bridge protons). The 1:1 stoichiometry of the complexes between **4** and the analytes shown in Table 1 was determined by the continuous variation method shown in the Job plot in Figure 2 for 2,4,7-trinitrofluorenone.

The Analytes. NMR titrations with seven guest molecules (nitro arenes) were carried out in $CDCl_3$, and the binding constants for the complexes were computed by least squares nonlinear fitting using the program EQNMR.[30] The results are shown in Table 1. A rather high binding constant of 490 M^{-1} was obtained for 2,4,7-trinitrofluorenone as guest which can be contrasted to the result obtained by Potluri and Maitra of 220 M^{-1} with a host molecule comprised of two pyrene plates bound together by a 7-deoxycholic acid type bridge via carboxylic ester hinges.[16]

We believe that the higher binding constant obtained with **4** can be ascribed to a tendency for this molecule to preorganize. A higher binding constant (675 M^{-1}) is obtained with a totally rigid molecule with fixed conformation as reported by Zimmerman.[20]

Overall the binding constants obtained are very similar to the values reported for different and more rigid receptor systems, suggesting that in the case of **4** the rigidity of the hinge region is large enough not to impinge on a strong interaction with guest molecules. The binding observed is due to the formation of charge-transfer complexes which is also evident from the dark red to brownish coloration of the resulting solutions. It is therefore not surprising that the binding constant in-

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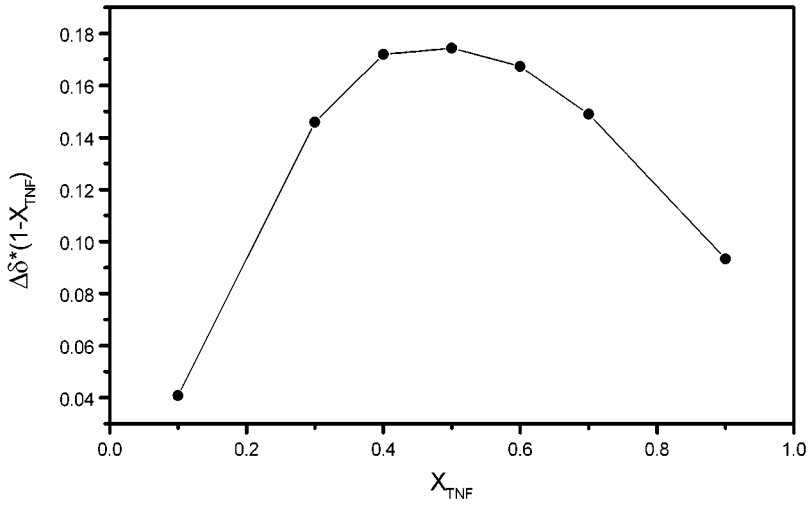

Figure 2. Job plot of the chemical shift change of the *N*-methyl groups of the tweezer molecule (**4**) as a function of the mole fraction of 2,4,7-trinitrofluorenone in $CDCl_3$ showing the 1:1 binding stoichiometry.

creases sharply with the number of electron-withdrawing groups present in the guest molecules. Minor effects on the substitution pattern of the dinitro benzenes may be noted. The *ortho*- and *meta*-compounds scarcely show any interaction with **4** while *p*-dinitrobenzene forms a definite complex albeit with a low binding constant of 6 M^{-1}. With one additional nitro group as in 1,3,5-trinitrobenzene the binding constant increases more than 30 times to 182 M^{-1}. Substitution of one of the three nitro groups with the less electron-withdrawing cyano group leads to a smaller binding constant of 55 M^{-1} underscoring the sensitivity of the charge-transfer interaction. The seemingly minor change of introducing a methyl group to obtain 2,4,6-trinitrotoluene again greatly reduces the binding constant by a factor of more than 7 times to 24 M^{-1}. This effect can only be explained in terms of steric hindrance. The X-ray crystal structure of 2,4,6-trinitrotoluene reveals that the methyl group forces the nitro groups out of plane with the central ring thus increasing the thickness. The torsion angles reported are in the range of 30° to 60°.[31,32] Close examination of the X-ray structure of **4** with 1,3,5-trinitrobenzene (Figure 1) shows a very tight fit between the host and guest. Compound **4** may not readily adapt to a somewhat thicker molecule-like 2,4,6-trinitrotoluene although it has approximately the same acceptor properties as 1,3,5-trinitrobenzene. The very high binding constant of 2,4,7-trinitrofluorenone may be ascribed to at least two factors. First, the electron-withdrawing nitro groups have been augmented by the carbonyl group. Second, the fused three-ring system is capable of a much larger overlap with the host 1-methylphenanthro[9,10-*d*]imidazol-2-yl groups.

Conclusions

In conclusion we have shown how a new and versatile receptor platform based on the concept of molecular tweezers is easily realized by means of a simple synthetic strategy. The crystal structures of both the neutral tweezer molecule and the tweezer molecule with bound 1,3,5-trinitrobenzene indicate that the molecular conformation might be preorganized and flexible enough to encompass slight differences in interplanar distances. Further we showed that the binding of planar nitroaromatic compounds is comparable to the very rigid tweezer molecules which has been reported as the compounds with the highest binding constants.

Experimental Section

2-(3-Bromophenyl)-1*H*-phenanthro[9,10-*d*]imidazole·AcOH (1). Phenanthrenequinone (42 g, 0.20 mol), 3-bromobenzaldehyde (36 g, 0.2 mol), and ammonium hydrogencarbonate (32 g, 0.40 mol) were mixed in glacial acetic acid (250 mL). Initially the mixture foamed due to the effervescence of CO_2(g). After this process had subsided, the mixture was refluxed for 1 h. During the reaction time, all solids dissolved, and then the product precipitated toward the end. Water (100 mL) was added carefully and the mixture cooled. The product was filtered, washed with water and a little hexane, and dried. This gave the acetate of **1** as colorless material in 82% yield (71 g). This product was used without further purification. Mp 174−175 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): δ 2.2 (s, 3H, CH_3), 7.2 (t, ^3J(H,H) = 8 Hz, 1H, ArH), 7.3 (s, 1H, ArH), 7.4 (d, ^3J(H,H) = 8 Hz, 1H, ArH), 7.5 (m, 4H, ArH), 7.9 (d, ^3J(H,H) = 8 Hz, 1H, ArH), 8.1 (s, 1H, ArH), 8.2 (m, 2H, ArH), 8.5 (m, 2H, ArH), 9.2 (bs, 2H, NH/OH); ^{13}C NMR (63 MHz, DMSO-d_6, 300 K, TMS): δ 21.9, 122.8, 123.1, 124.6, 125.0, 125.9, 126.2, 126.3, 126.4, 127.7, 128.0, 128.5, 128.7, 129.2, 132.0, 132.6, 133.4, 137.9, 148.2, 172.8 (two signals are missing which is ascribed to accidental isochrony). Anal. Calcd for $C_{23}H_{17}BrN_2O_2$: C, 63.75; H, 3.95; N, 6.47. Found: C, 64.13; H, 5.64; N, 6.63.

2-(3-Bromophenyl)-1-methyl-phenanthro[9,10-*d*]imidazole (2). Compound **1** (69.5 g, 0.16 mol) was suspended in THF (1400 mL), and *t*BuOK (53 g, 0.47 mol) was added. The mixture was stirred for 20 min, and methyl iodide (79.5 g, 0.56 mol) was added. A precipitate formed, and the mixture was stirred for 1 h more. Water (10 mL) was then added and the mixture evaporated to dryness. Water (200 mL) and chloroform (enough to dissolve all the solids) was added. The organic phase was separated, dried ($MgSO_4$), and evaporated to dryness leaving the crude product. Recrystallization from ethanol gave compound **2** as a thin colorless needles in 74% yield (45.9 g). Mp 167−168 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 300 K, TMS): δ 4.2 (s, 3H, CH_3), 7.4 (t, ^3J(H,H) = 8 Hz, 1H, ArH), 7.5−7.7 (m, 6H, ArH), 7.9 (s, 1H, ArH), 8.3−8.4 (m, 1H, ArH), 8.6 (d, ^3J(H,H) = 8 Hz,1H, ArH), 8.7 (t, ^3J(H,H) = 8 Hz, 2H, ArH); ^{13}C NMR (63 MHz, $CDCl_3$, 300K, TMS): δ 36.7, 121.3, 123.2, 123.5, 123.7, 124.1, 125.0, 125.6, 126.2, 127.3, 127.92, 127.95, 128.4, 128.7, 129,0. 129.9, 130.8, 133.10,

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133.13, 133.5, 138.2, 151.5. Anal. Calcd for $C_{22}H_{15}BrN_2$: C, 68.23; H, 3.90; N, 7.23. Found: C, 67.87; H, 3.68; N, 7.20.

3-(1-Methylphenanthro[9,10-*d*]imidazol-2-yl)-phenylboronic Acid hydrochloride (3). Compound **2** (25 g, 64 mmol) was dissolved in dry THF (400 mL) under argon and cooled to ←70 °C with a CO_2(s)/acetone bath. *n*BuLi (1.6 M, 60 mL, 96 mmol) was added. Triisopropyl borate (24.5 g, 0.13 mol) was added, the cooling bath was removed, and the mixture was left to stand for 2 h. HCl(aq) 20% 200 mL was added, and stirring was continued for 0.5 h. The mixture was evaporated until most of the THF had been removed. The product was filtered after cooling to ambient temperature, washed with light petroleum, and dried. The crude product was dried at a temperature <50 °C. The crude product was dissolved in a small amount of DMSO and precipitated with ether. This gave **3** as a colorless powder in 94% yield (23.5 g). Mp 239−241 °C; ^{1}H NMR (250 MHz, DMSO-d_6, 300 K, TMS): δ 4.4 (s, 3H, CH_3), 7.7−7.9 (m, 5H, ArH), 8.0 (d, ^3J(H,H) = 8 Hz, 1H, ArH), 8.2 (d, ^3J(H,H) = 8 Hz, 1H, ArH), 8.4 (s, 1H, ArH), 8.7 (d, ^3J(H,H) = 8 Hz,1H, ArH), 8.8 (d, ^3J(H,H) = 8 Hz, 1H, ArH), 8.9 (d, ^3J(H,H) = 8 Hz,1H, ArH), 9.0 (d, ^3J(H,H) = 8 Hz, 1H, ArH); ^{13}C NMR (63 MHz, DMSO-d_6, 300 K, TMS): δ 37.9, 122.3, 123.0, 123.4, 123.6, 125.0, 125.6, 127.1, 128.0, 128.6, 128.9, 129.0, 129.1, 129.4, 129.9, 133.1, 137.1, 138.4, 138.5, 150.1 (the signals from two of the carbon atoms could not be observed. This is ascribed to either accidental isochrony or to the carbon bonded to boron). Anal. Calcd for $C_{22}H_{18}BClN_2O_2$: C, 67.99; H, 4.67; N, 7.21. Found: C, 67.78; H, 4.57; N, 7.28.

2,6-Bis(3-(1-methyl-phenanthro[9,10-*d*]imidazol-2-yl)-phenyl)pyridine (4). 2,6-Dibromopyridine (1.2 g, 5 mmol), compound 3 (4.3 g, 11 mmol), water (100 mL), toluene (100 mL), dimethoxyethane (100 mL), Na_2CO_3 (12 g, 0.11 mol), and $(Ph_3P)_2PdCl_2$ (0.25 g, 0.35 mmol, 3.5 mol %) were mixed in a (500 mL) conical flask and degassed with argon. The mixture was refluxed overnight under argon. The following day a white solid had precipitated. The mixture was evaporated to 100 mL, cooled, and filtered. The product was washed with ether and light petroleum. The crude product was dissolved in chloroform and precipitated with ether, giving compound **4** as a white powder in 93% yield (3.2 g). Mp 273−275 °C; ^{1}H NMR (250 MHz, CDCl3, 300 K, TMS): δ 4.3 (s, 3H, CH_3), 7.4−7.7 (m, 10H, ArH), 7.8−7.9 (m, 5H, ArH), 8.2 (d, ^3J(H,H) = 8 Hz, 2H, ArH), 8.3 (d, ^3J(H,H) = 8 Hz, 2H, ArH), 8.6 (d, ^3J(H,H) = 8 Hz, 2H, ArH), 8.6−8.8 (m, 6H, ArH); ^{13}C NMR (250 MHz, $CDCl_3$, 300 K, TMS): δ 36.5, 119.6, 120.9, 122.9, 123.4, 124.0, 124.7, 125.2, 125.8, 126.9, 127.6, 127.7, 128.1, 128.3, 128.5, 129.1, 129.5, 129.6, 130.8, 131.4, 137.9, 138.2, 140.3, 152.9, 156.5. Anal. Calcd for $C_{49}H_{33}N_5$: C, 85.07; H, 4.81; N, 10.12. Found: C, 83.81; H, 4.73; N, 9.94.

Crystallography. General crystallographic data can be found in Table 2. The crystals **4** and **4**·TNB were drawn directly from the mother liquor, coated with a thin layer of protecting oil, mounted on glass fibers using Apiezon grease, and transferred quickly to the cold stream of nitrogen (Oxford Cryostream) on the diffractometer (Siemens SMART CCD Platform).

Table 2. Crystallographic Data for Compound 4 and for the 1:1 Complex of 4 and 1,3,5-Trinitrobenzene

compound	**4**	**4**:(1,3,5-trinitrobenzene)
formula	$C_{49}H_{33}N_5$	$C_{56}H_{38}N_8O_6Cl_2$
formula wt	691.80	989.84
crystal system	triclinic	triclinic
space group	$P-1$	$P-1$
Z	2	2
a, Å	10.835(2)	10.1412(15)
b, Å	11.104(2)	10.5079(16)
c, Å	14.063(3)	24.330(4)
α,^{o}	91.093(4)	84.990(4)
β,^{o}	93.404(4)	79.243(3)
γ,^{o}	101.956(4)	63.291(3)
V, Å^3	1651.4(5)	2275.3(6)
ρ, g cm^3	1.391	1.445
crystal dimensions, mm	0.38 × 0.25 × 0.13	0.37 × 0.12 × 0.12
type of radiation	Mo−Kα	Mo−Kα
μ, cm^{-1}	0.083	0.209
T, K	120(2)	120(2)
number of reflections	22171	29973
unique reflections	9104	12358
$R(F)$, $R_w(F^2)$ all data	0.0632, 0.1674	0.1222, 0.3423

Crystals of **4**·TNB lost solvent upon exposure to air, and this impaired the quality of the data due to a degradation of the crystalline properties. An almost complete sphere of reciprocal space was covered by a combination of several sets of exposure frames; each set with a different φ angle for the crystal, and each frame covering a scan of 0.3° in ω. Data collection, integration of frame data, and conversion to intensities corrected for Lorenz, polarization, and absorption effects were performed using the programs SMART,[33] SAINT,[33] and SADABS.[34] Structure solution, refinement of the structures, structure analysis, and production of crystallographic illustrations were carried out using the programs SHELXS97,[35] SHELXL97,[35] and SHELXTL.[36] The structures were checked for higher symmetry and none was found.[37] In both of the structures H atoms were included in their calculated positions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-156564 and CCDC-156565. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223−336−033; e-mail: deposit@ccdc.cam.ac.uk).

JO015690J

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(34) Empirical absorption program (SADABS) written by George Sheldrick for the Siemens SMART platform.

(35) SHELX-97, Program for structure solution and refinement written by George M. Sheldrick, 1997.

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