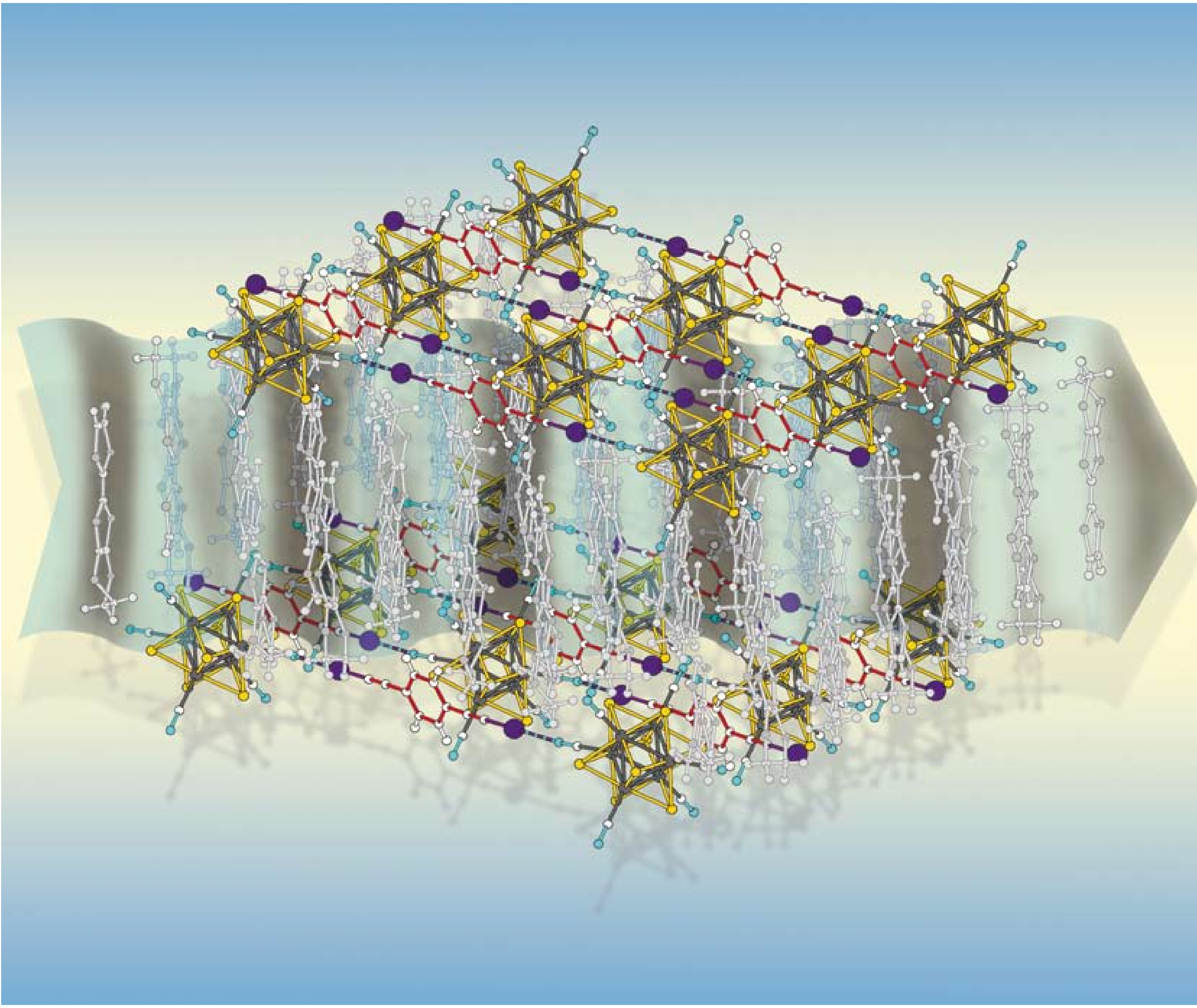
ChemComm

Chemical Communications

www.rsc.org/chemcomm

Number 19 | 21 May 2008 | Pages 2169–2276



ISSN 1359-7345

COMMUNICATION
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1359-7345(2008)19;1-0

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The 8 : 1 : 1 ternary hybrid framework in the system $[\text{EDT-TTF}^{\bullet +}][\text{1,4-bis(iodoethynyl)benzene}][Re_6Se_8(CN)_6]^{4-}$: dual noncovalent expression of the octahedral halogen-bond hexa-acceptor nanonode†

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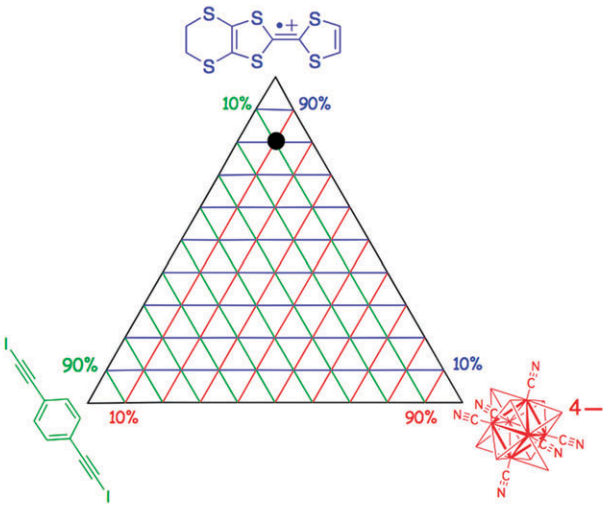
Received (in Cambridge, UK) 14th January 2008, Accepted 31st March 2008
First published as an Advance Article on the web 8th April 2008
DOI: 10.1039/b800571k

Complementary shapes of the neutral symmetrical halogen-bond bis-donor core and octahedral inorganic cluster core prevent halogen-bonded polymers developing in more than one direction, favouring further templating by conducting radical cation slabs and yielding an 8 : 1 : 1 phase formulation instead of *n* : 2 : 1, with a 2D net, or *m* : 3 : 1, with a pseudo-cubic architecture, which may in principle also be targeted.

$[\text{EDT-TTF}^{\bullet +}]_8[\text{1,4-bis(iodoethynyl)benzene}][Re_6Se_8(CN)_6]^{4-}$ (EDT-TTF is ethylenedithiotetrathiafulvalene), reported herein, is the first compound discovered in an exploration of the phase diagram of ternary hybrid frameworks (THF) of general formulation (organic radical cation$^{\bullet +}$)–multiple halogen-bond donor neutral linkage–$[Re_6Se_8(CN)_6{}^{4-/3-\bullet}]$, illustrated in Scheme 1, where the inorganic cluster anion is isosteric to C_{60}. In addition to looking for opportunities for both space partition and electronic structure modulation in ternary molecular solids, a complementary objective is to search for diversity[1] in the dimensionality of hybrid halogen-bonded frameworks, as either an *n* : 1 : 1 phase with one-dimensional halogen-bond topology, as achieved herein, an *n* : 2 : 1 phase with a 2D net, or an *n* : 3 : 1 phase with a pseudo-cubic architecture may in principle be targeted. All of the former unprecedented stoichiometries and phase formulations are expected to modulate the electron count, electronic structure dimensionality and physics of such conducting hybrid ternary phases.

In the course of one single experiment, electrocrystallization allows for the generation of carriers and their stabilization by intermolecular delocalization over long distances within stacks or slabs; and the electrostatic self-assembly/auto-templating of the former into bi-continuous O–I hybrid frameworks.[2] It has recently been extended further to the halogen-bonded co-assembly of *ternary* systems by engaging neutral functional π-conjugated spacers, as illustrated by deliberate introduction of halogen-bond multi-donor neutral linkages, providing an entry into the phase diagram of ternary metallic constructs like β″-$(\text{BEDT-TTF})_3{}^{\bullet +}[\text{1,4-bis(iodoethynyl)benzene}][Cl^-]$, and a modulation of their interface and electronic structure.[3] Besides, the self-assembly of the octahedral halogen-bond hexa-acceptor anionic clusters, $[Re_6Se_8(CN)_6{}^{(4-/3\bullet -)}]$ with *charged* symmetrical halogen-bond linkages, be they single radical cation, *E*-TTF–$I_2{}^{\bullet +}$, or mixed valence dimers, $(\text{EDT-TTF–I})_2{}^{\bullet +}$, was recently reported[4] to direct the construction of $[PPh_4{}^+]_2\{[E\text{-TTF–}I_2{}^{\bullet +}][Re_6Se_8(CN)_6{}^{3-}]$ and $[PPh_4{}^+]_2[\text{EDT-TTF–I}]_2{}^{\bullet +}[\text{EDT-TTF–I}]^{\bullet +}[Re_6Se_8(CN)_6{}^{4-}]\}$ upon allowing for strong C_{sp2}–I···N≡C–Re self-complementary halogen-bonds to develop into infinite motifs, yet in one direction only. We now report how *neutral*, symmetric halogen-bond donor linkages express the octahedral halogen-bond hexa-acceptor nanonode into an 8 : 1 : 1 ternary hybrid framework where a single polymeric halogen-bonded hybrid interface has been favoured yet again.

Electrocrystallization[5] in a two-compartment cell at a constant current of 0.5 μA and 298 K for 2 weeks of EDT-TTF[6] (6 mg) in a mixture of CH_3CN–THF (12 : 2, v/v) containing 1,4-bis(iodoethynyl)benzene[7] and $(PPh_4)_4[Re_6Se_8(CN)_6]$[8] (10 and 25 mg, respectively) affords shiny black crystals of $(\text{EDT-TTF})_8[\text{1,4-bis(iodoethynyl)benzene}][Re_6Se_8(CN)_6]$ whose



Scheme 1

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† Electronic supplementary information (ESI) available: Fig. ESI 1 and 2, and crystallographic data in CIF format. CCDC 674025 and 674026. See 10.1039/b800571k

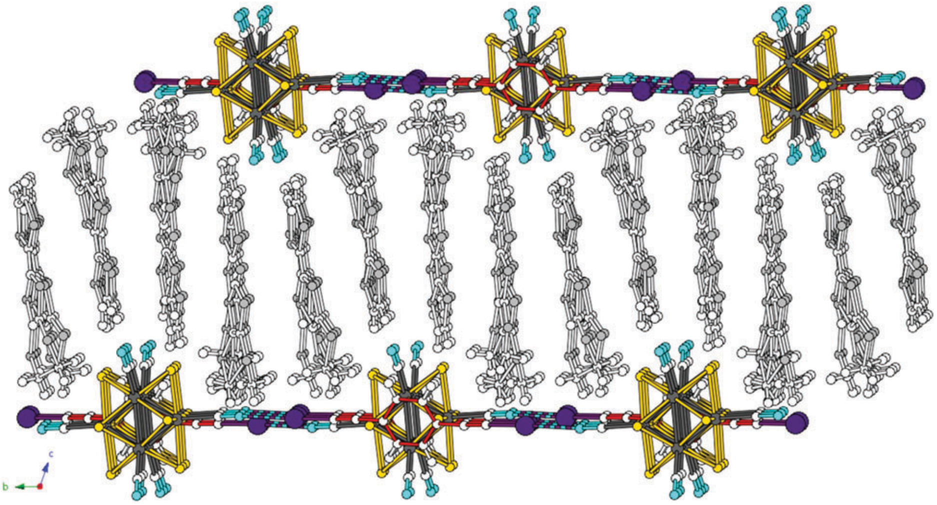

Fig. 1 The dual templating ability of [Re$_6$Se$_8$(CN)$_6$$^{4-}$] is illustrated here by its expression into both the halogen-bond polymers developing along *b* and the van der Waals fit of the complementary shapes of the aromatic and cluster cores,[11] located both about independent inversion centres and effectively screening the charge of the inorganic node along *a*. Note that the dissymmetry of EDT-TTF appears to be advantageous in modulating the slab envelop to actually position a hollow receptacle for the protruding cyanides while, in turn, flexible ethylenedithio end-group C–H bond donors reach out towards halogen atoms.

formulation was obtained by determination of their crystal structure.‡

As exemplified in Fig. 1, a layered construct is obtained where radical cation single slabs alternate with 1 : 1 anionic hybrid [1,4-bis(iodoethynyl)benzene][Re$_6$Se$_8$(CN)$_6$]$^{4-}$ slabs. Note that two out of the three pairs of symmetrical cyanide ligands on any cluster core remain uninvolved and are left to protrude out at the interface. Fig. 1 also provides a first glance at the linear halogen-bond polymer as well as an appreciation of the striking fit of the benzene cores effectively screening each cluster four negative charges along *a*, as exemplified in Fig. 2a. Note the similarity of the topology of the anionic hybrid slab within (EDT-TTF)$_8$$^{4(\bullet+)}$[1,4-bis(iodoethynyl)-benzene][Re$_6$Se$_8$(CN)$_6$]$^{4-}$ (Fig. 2a) with that achieved earlier for [PPh$_4$$^+$]$_2${[*E*-TTF–I$_2$]$^{\bullet+}$[Re$_6Se_8(CN)_6$]$^{3-}$}, shown in Fig. 2b.

The donor layers of [EDT-TTF]$_8$$^{4(\bullet+)}$[1,4-bis(iodoethynyl)-benzene][Re$_6$Se$_8$(CN)$_6$]$^{4-}$ contain 14 different donor–donor interactions. According to the calculated $\beta_{\text{HOMO–HOMO}}$ interaction energies there are four strong interactions along the stacks along *b* one of which is somewhat smaller (0.658, 0.702, 0.648 and 0.450 eV) and weaker interstack interactions (0.122–0.002 eV). That is, the radical cation slab develops primarily based on collections of tetramers strongly interacting along the stacks. With eight donor molecules per repeat unit of the layer there are eight HOMO bands and for a 4$^-$ anion, two bands are empty. As the band structure[9] (Fig. 3a) for the donor layer shows the presence of an energy gap separating the two upper bands, the compound is expected to be a pseudo-1D semiconductor, as observed. Single crystal four-point conductivity measurements confirm the activated conductivity ($\sigma_{300\text{ K}}$ = 2.5 S cm^{-1}, Fig. 3b).

Note finally that the C–I bond length increases from 2.007(7) Å in the single component solid† 1,4-bis(iodoethynyl)benzene up to 2.035(11) Å for the same molecule embedded in the ternary title phase, an indication that some amount of covalency involving the nitrogen lone pair and the antibonding $\sigma_{\text{C–I}}$* orbital, if any, would complement the

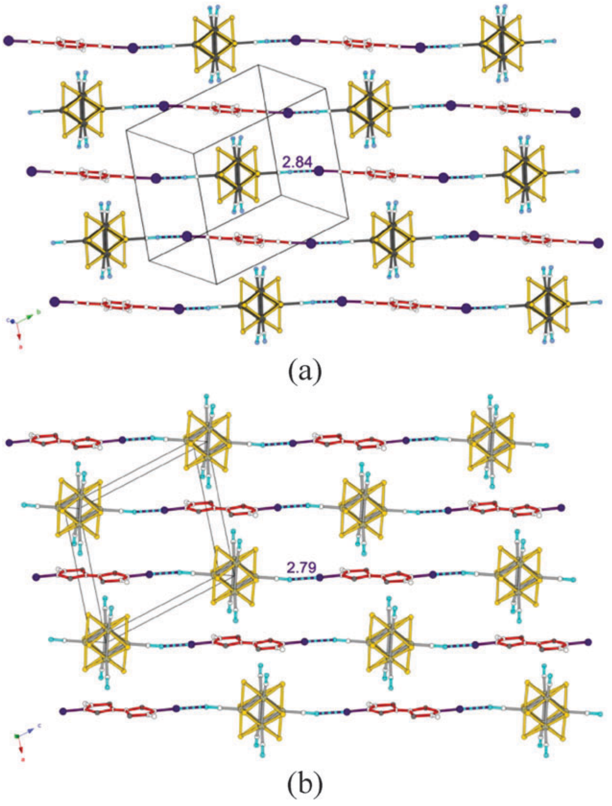

Fig. 2 Illustration of the striking similarity between the 2D non-covalent networks in (a) [EDT-TTF]$_8$$^{4(\bullet+)}$[1,4-bis(iodoethynyl)-benzene] [Re$_6$Se$_8$(CN)$_6$]$^{4-}$, and (b) [PPh$_4$$^+$]$_2${[*E*-TTF–I$_2$$^{\bullet+}$]-[Re$_6Se_8(CN)_6$$^{3-}$]}. The short[4,5] I···N bond length values are indicated. Note that, in the context of framework solids, the use of a neutral linkage instead of [*E*-TTF–I$_2$]$^{\bullet+}$ was expected to minimize charge densification and favor the stabilization of *n* : 2 : 1 or *n* : 3 : 1 phases, with 2 or 3D frameworks, respectively, instead of the observed 8 : 1 : 1 formulation.

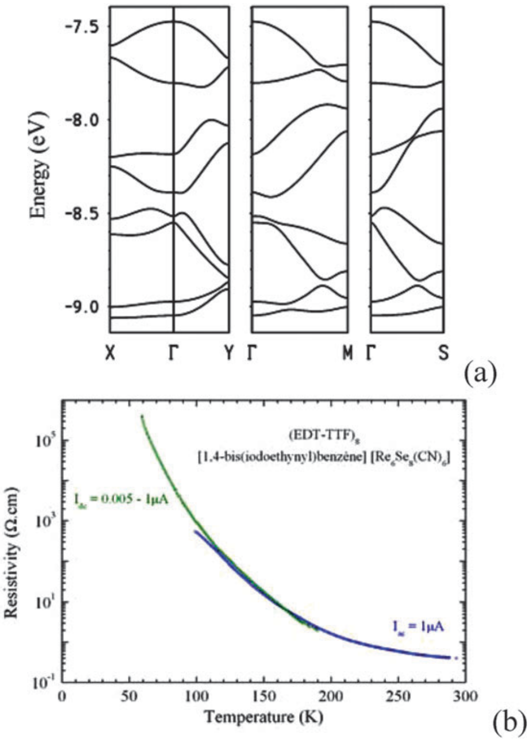

Fig. 3 (a) Band structure of [EDT-TTF]$_8$[1,4-bis(iodoethynyl) benzene][Re$_6$Se$_8$(CN)$_6$], Γ = (0, 0), X = (a*/2, 0), Y = (0, b*/2, 0), M = (a*/2, b*/2) and S = ($-a$*/2, b*/2); (b) Temperature dependence of the resistivity of [EDT-TTF]$_8$[1,4-bis(iodoethynyl)benzene][Re$_6$Se$_8$(CN)$_6$].

primarily electrostatic C–I$^{\delta+}\cdots{}^{-}$NC–Re halogen-bonding interaction. This is also consistent with the observation that all three weak interfacial C–I$^{\delta+}\cdots{}^{\delta-}$I–C halogen-bond interactions identified in 1,4-bis(iodoethynyl)benzene (4.10, 4.24 and 4.45 Å, Fig. ESI 2†) are considerably weaker than the C–I$^{\delta+}\cdots{}^{-}$NC Re halogen bonds shown in Fig. 2. A comparison with the bonding pattern in β″-(BEDT-TTF)$_3{}^{\bullet+}$[1,4-bis(iodoethynyl)benzene][Cl$^-$] indicates that here, the C–I bond length in C–I$^{\delta+}\cdots{}^{-}$Cl also increases up to 2.042(10) Å upon charge-assisted halogen bonding. This adds to the current debate on the unsettled issue of a covalent component in halogen-bond interactions.[10]

To summarize (Fig. ESI 1†), three types of noncovalent interactions are found to direct the topology of the present 8 : 1 : 1 ternary hybrid framework. One is a strong C–I$\cdots$N$\equiv$C–Re halogen-bond which governs the self-assembly developing into a one-dimensional polymer out of the octahedral inorganic node; another is the physical, van der Waals embrace of the complementary shapes of the flat, symmetrical neutral aromatic cores and that of the cluster anion.[11] The third noncovalent interactions are the HOMO–HOMO interactions within and between stacks of radical cation tetramers stabilizing the conducting slabs and allowing for charge carriers delocalization.

Current work focuses on developing this generic phase diagram further by engaging neutral molecular polyhalogen-bond donor spacers with no symmetry, thereby aiming to counteract the physical aromatic core–cluster hybrid fit. This may offer opportunities for creating a zero-gap conductor by promoting slight modifications of the intertetramers interactions sizeable enough to close the minute, 0.08 eV energy gap in the band structure of Fig. 3a. Analysis of the band structure suggests that the gap may disappear by decreasing the intratetramer interactions or/and by increasing the intertetramer interactions.

We acknowledge support from the CNRS, the program ANR CHIRASYM 2005-08 (NT05-2 42710), the Spanish Ministerio de Educación y Ciencia (Project FIS2006-12117-C04-01) and Generalitat de Catalunya (2005 SGR 683). Jean-Charles Ricquier is kindly acknowledged for his help in preparing Fig. ESI 1.

Notes and references

‡ For both structures, data were collected on a Bruker four-circle diffractometer attached with a CCD area detector and a graphite monochromator for the MoK radiation (50 kV, 30 mA) λ = 0.71073 Å at 293(2) K. Absorption correction was applied using the SADABS program (Siemens, USA, 1995). Crystal structure analysis for (EDT-TTF)$_8$[1,4-bis(iodoethynyl)benzene][Re$_6$Se$_8$(CN)$_6$], $C_{80}H_{52}I_2N_6Re_6S_{48}Se_8$, triclinic, space group $P\bar{1}$, a = 12.8888(15) Å, b = 14.3359(10) Å, c = 18.486(2) Å, α = 105.199(7)°, β = 100.579(7)°, γ = 106.384(8)°, V = 3037.6(6) Å^3, D = 2.54 g cm^{-1}, Z = 1. Black plate-like crystal, 0.2 × 0.1 × 0.05 mm. A total of 106 829 reflections were collected up to θ = 30.03° of which 17 639 are independent among 9600 observed [$F_o > 4\sigma(F_o)$]. The structure solution (SHELXS-97) and refinements on $F_o{}^2$ (SHELXL-97) gave R(obs.) = 0.0485 [R(all) = 0.126] and Rw(obs.) = 0.090 [Rw(all) = 0.111] for 694 parameters; min and max residual electron densities were 2.223 and −1.737 e Å^{-3}. CCDC 674025.†
Crystals of 1,4-bis(iodoethynyl)benzene were obtained by slow evaporation of a dichloromethane–hexane solution. Crystal structure analysis for $C_{10}H_4I_2$, monoclinic, space group $P21/n$, a = 4.2376(3) Å, b = 17.3316(13) Å, c = 7.1027(5) Å, β = 95.632(7)°, V = 519.14(6) Å^3, D = 2.418 g cm^{-1}, Z = 2. Yellow plate-like crystal, 0.2 × 0.1 × 0.05 mm. A total of 6704 reflections were collected up to θ = 27.5° of which 1198 are independent among 605 observed [$F_o > 4\sigma(F_o)$]. The structure solution (SIR-92) and refinements on $F_o{}^2$ (SHELXL-97) gave R(obs.) = 0.0456 [R(all) = 0.131] and R(obs.) = 0.056 [Rw(all) = 0.067] for 55 parameters; min and max residual electron densities were 0.726 and −0.673 eÅ^{-3}. CCDC 674026.†

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