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Erstveröffentlichung in / First published in:

Journal of the American Chemical Society. 2020, 142 (43), S. 18293–18298. ACS Publications. ISSN 1520-5126.

DOI: <https://doi.org/10.1021/jacs.0c07013>

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A Curved Graphene Nanoribbon with Multi-Edge Structure and High Intrinsic Charge Carrier Mobility

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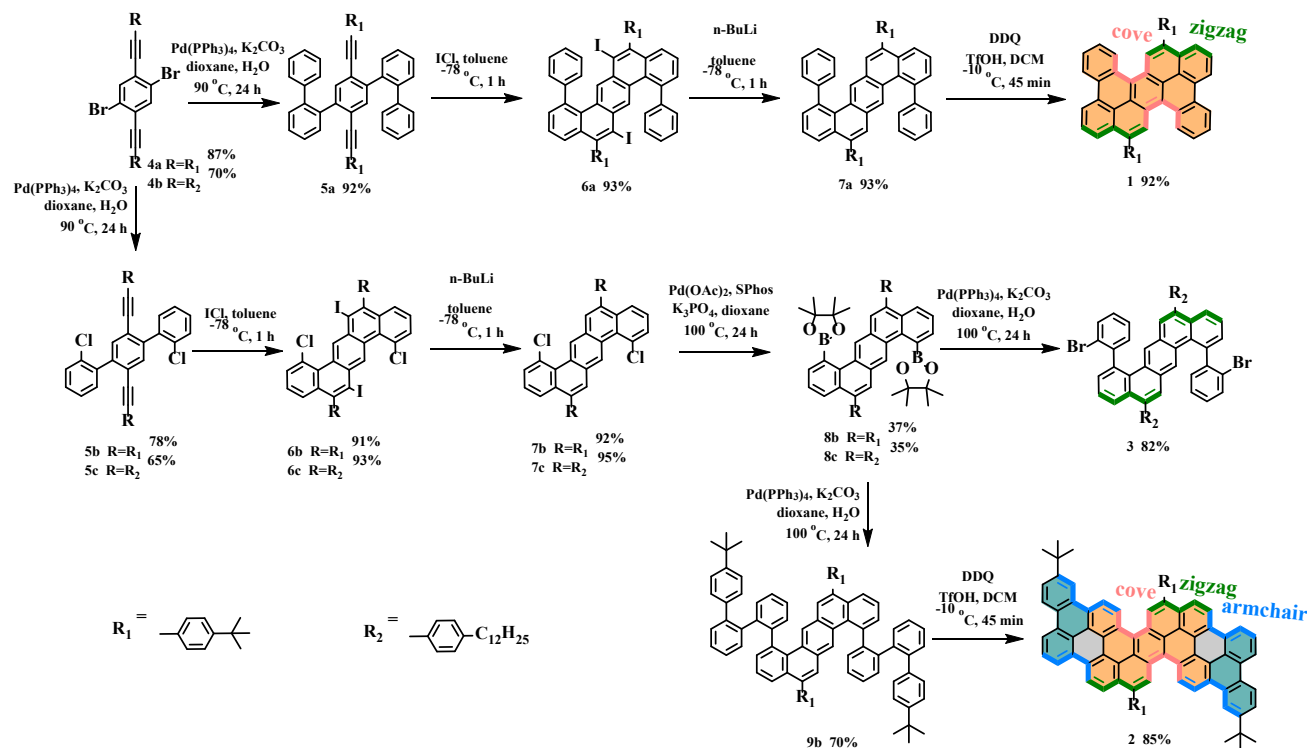
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ABSTRACT: Structurally well-defined graphene nanoribbons (GNRs) have emerged as highly promising materials for the next-generation nanoelectronics. The electronic properties of GNRs critically depend on their edge topologies. Here, we demonstrate the efficient synthesis of a curved GNR (**cGNR**) with a combined cove, zigzag, and armchair edge structure, through bottom-up synthesis. The curvature of the **cGNR** is elucidated by the corresponding model compounds tetrabenzo[*a,cd,j,lm*]perylene (**1**) and diphenanthrene fused tetrabenzo[*a,cd,j,lm*]perylene (**2**), the structures of which are unambiguously confirmed by the X-ray single crystal analysis. The resultant multi-edged **cGNR** exhibits a well-resolved absorption at the near-infrared (NIR) region with a maximum peak at 850 nm, corresponding to a narrow optical energy gap of ~1.22 eV. Employing THz spectroscopy, we disclose a long scattering time of ~60 fs, corresponding to a record intrinsic charge carrier mobility of ~600 cm² V⁻¹ s⁻¹ for photogenerated charge carriers in **cGNR**.

Atomically precise graphene nanoribbons (GNRs) have attracted significant attention in recent years due to their fascinating electronic properties and potential applications in nano-electronic devices¹⁻⁶. Both theoretical and experimental studies have demonstrated that the electronic and magnetic properties of GNRs are critically dependent on their widths and edge topologies⁷⁻⁸. Therefore, the synthesis of atomically precise GNRs with controlled energy gaps is highly desirable not only for their fundamental physiochemical studies but also for their promising applications in carbon-based nanoelectronics⁹⁻¹². In contrast to armchair edged GNRs (AGNRs) displaying semiconducting property with a direct energy gap¹³, zigzag edged GNRs (ZGNRs) typically exhibit narrow bandgaps and localized edge states¹⁴⁻¹⁵. The structurally defined AGNRs have been successfully synthesized in the last decade¹⁶⁻²¹, while the ZGNRs remained less explored due to the highly unstable zigzag edges. In addition, cove edged GNRs with unique curved geometry are attractive because they can exhibit improved dispersibility in solution, and provide an additional means to control the optoelectronic properties of GNRs^{7,22-23}.

Thereby, the combination of armchair, cove, and zigzag edge structures can impart GNRs with unique geometries and physiochemical properties that are not accessible by those with solely one type of edge structures.

Here, we demonstrate the first solution synthesis of a curved GNR (**cGNR**) with a combined cove, zigzag and armchair edge structure, which possesses a width of 0.7 nm and an average length of 23 nm. Two model compounds as the subunits of the **cGNR**, namely tetrabenzo[*a,cd,j,lm*]perylene (**1**) and diphenanthrene fused tetrabenzo[*a,cd,j,lm*]perylene (**2**) containing a double [4]helicene unit (Scheme 1), are synthesized. Single-crystal structures of **1** and **2**, along with the density functional theory (DFT) simulation clearly elucidate the curvature of the corresponding **cGNR**. The **cGNR** exhibits a well-resolved absorption in the near-infrared (NIR) region with a maximum peak at ~850 nm. To date, this is the longest wavelength among the reported solution-processable GNRs^{17,21,24-26}, corresponding to a quite narrow optical energy gap of 1.22 eV for this **cGNR**, slightly higher than the lowest bandgap of 1.03 eV reported for solution-based



Scheme 1. Schematic illustration of the synthesis of **1**, **2** and **3**.

GNRs²¹. Employing contact-free terahertz (THz) spectroscopy, we demonstrate that the **cGNR** possesses a record-high intrinsic carrier mobility of up to $\sim 600 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, making it a promising material for optoelectronic devices²⁷. Our study provides a strategy to simultaneously achieve a narrow width, good dispersibility, low bandgap, and high carrier mobility for GNRs by introducing a multi-edge structure.

Firstly, model compounds **1** and **2**, which can be regarded as the short segments of **cGNR**, and monomer 1,8-bis(2-bromophenyl)benzo[*k*]tetrathene (**3**) for the GNR, were synthesized (Scheme 1). Compound 4,4'-((2,5-dibromo-1,4-phenylene)bis(ethyne-2,1-diyl))bis(*tert*-butylbenzene) (**4a**) was synthesized from 1,4-dibromo-2,5-diiodobenzene via Sonogashira coupling in 87% yield (Scheme S1). A Suzuki coupling of **4a** with 2-biphenylboronic acid gave 1,4-bis(2'-biphenyl)-2,5-bis(4-(*tert*-butyl)-phenyl)ethynylbenzene (**5a**) in 92% yield. ICl₄-mediated benzannulation afforded 5,12-bis(4-(*tert*-butyl)phenyl)-6,13-diiodo-1,8-diphenylbenzo[*k*]tetrathene (**6a**) in 93% yield. After the treatment of **6a** with *n*-butyllithium, 5,12-bis(4-(*tert*-butyl)phenyl)-1,8-diphenylbenzo[*k*]tetrathene (**7a**) was synthesized in 93% yield. Then, compound **1** was achieved through the Scholl reaction of **7a** in 92% yield. Following the similar synthetic strategies, compound **2** and monomer **3** were successfully synthesized with the yields of 82% and 85%, respectively (see details in the Supporting Information).

The chemical identities of **1** and **2** were confirmed via high-resolution mass spectrometry (HR-MS) (Figure S1) and NMR analysis (Figure S2-S11). Notably, compound **2** exhibits a significant tendency to form aggregates after dissolution in 1,1,2,2-tetrachloroethane-*d*₂, resulting in a slow increase of ¹H NMR signal width. This effect can be reversed by heat treat-

ment and dilution (Figure S11). Besides, the crystals of **1** and **2** were grown by slow evaporation of their solutions in methanol/dichloromethane (DCM) and *n*-hexane/carbon disulfide, respectively, allowing to reveal their structural features by the X-ray single-crystal analysis (Figure 1). Both **1** and **2** adopt perfect centrosymmetric structures, and their (*P*, *P*) and (*M*, *M*) enantiomers present in a ratio of 1:1 in the solid-state. Both **1** and **2** manifest a curved geometry due to the steric repulsion of hydrogen atoms of the double [4]helicene segments (Figure 1). The dihedral angle between plane C1-C2-C3 and plane C3-C4-C5 is 38.7° in **1** (Figure 1a), which is slightly larger than that of **2** (36.5°, Figure 1b) and well comparable with those of the reported double [4]helicenes²².

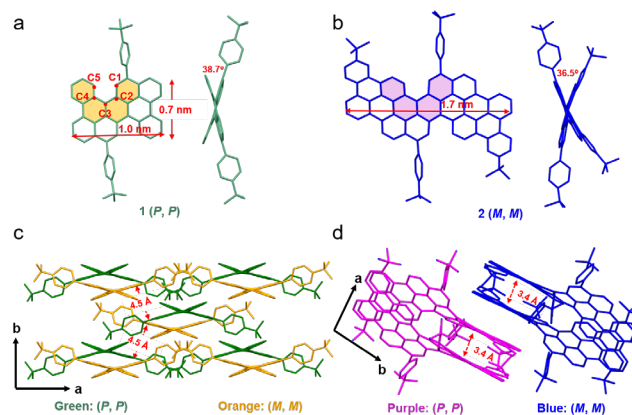
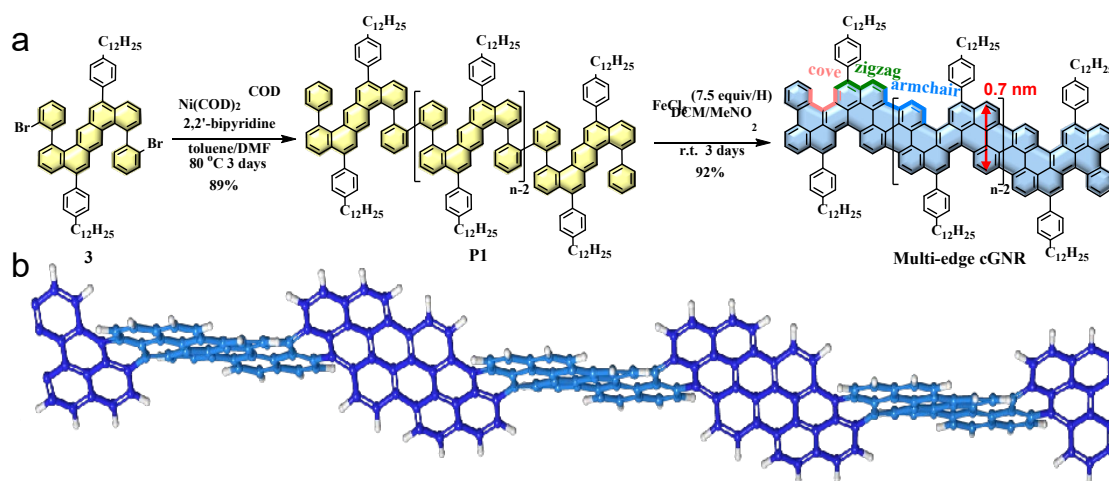


Figure 1. X-ray crystal structures of **1** and **2**. All hydrogen atoms and solvent molecules are omitted for clarity. (a, b) Top and side views of **1** (*P*, *P*) and **2** (*M*, *M*). (c, d) Crystal packing of **1** and **2**.



Scheme 2. Synthetic route towards cGNR (a) and the geometry of cGNR by DFT simulation (b).

The synthesis of cGNR is illustrated in Scheme 2a. First, monomer **3** was synthesized from 1,4-dibromo-2,5-diiodobenzene over 8 steps (Scheme 1). Second, the poly(diphenyl benzo[k]tetraphene) (**P1**) substituted with dodecylphenyl groups was prepared by the AA-type Yamamoto polymerization of **3** (Scheme 2a). Gel permeation chromatography (GPC) analysis against linear polystyrene standard revealed that the number-average molecular weight (M_n) of the **P1** is around 18,100 g mol⁻¹ with a narrow dispersity of 1.15 (Figure S12). The MS spectrum of the resultant **P1** displays that the m/z intervals are well consistent with the exact mass of repeating unit diphenyl benzo[k]tetraphene (917 g mol⁻¹) (Figure S13). Finally, cGNR was obtained through the Scholl reaction of **P1** with FeCl_3 (7.5 equiv./H) as the Lewis acid and oxidant in DCM for 3 days. The resultant cGNR possesses a combined cove, zigzag and armchair edge structure with a width of 0.7 nm (Scheme 2a). The estimated average length of cGNR is about 23 nm based on the M_n of **P1** (Figure S12b).

The successful cyclodehydrogenation of **P1** was firstly demonstrated by Fourier transform infrared (FTIR) (Figure 2a) and Raman (Figure 2b) investigations. FTIR spectrum of the cGNR revealed a significant attenuation of the bands from aromatic C-H stretching vibrations at 3052 and 3020 cm⁻¹ after the oxidative cyclodehydrogenation, with respect to the spectrum of the **P1**, suggesting the efficient graphitization²⁸ (Figure 2a). The successful formation of cGNR was further confirmed by solid-state NMR measurements (Figure S15-S16). The comparison of the ¹H NMR magic-angle spinning (MAS) spectra (Figure S15) of **P1** and cGNR demonstrated a clear increase in ¹H linewidth after graphitization. Moreover, the reduced π - π stacking of the cGNR can be identified in the 2D ¹H-¹H double-quantum single-quantum (DQ-SQ) NMR correlation spectrum (Figure S15). The ¹H-¹H auto-correlation signals of the aromatic protons fall in a much narrower range compared to other structurally similar GNRs²⁷. The narrower range of ¹H chemical shifts is a clear indication of reduced π - π stacking effects in the cGNR, which can be attributed to the non-planar nature of cGNR. The Raman spectrum of the cGNR exhibits a multi-component D band at 1300 cm⁻¹ and G band at 1597 cm⁻¹. Combination and high-order modes are identified at 2506, 2835, and 3169 cm⁻¹ (Figure 2b). Clear differences with in-plane GNRs are seen by performing multi-wavelength Raman spectroscopy: first, the D and G bands split into several components when using a laser excitation

energy of 1.96 eV, possibly due to resonant effects associated with the unique structure of cGNR (Figure S17-20)^{29,30}; second, the G peak shows a dispersion of ~27 cm⁻¹/eV (Figure S19b), which is much higher than that reported for in-plane GNRs, possibly deriving from the disruption of the aromatic core of the non-planar ribbons.

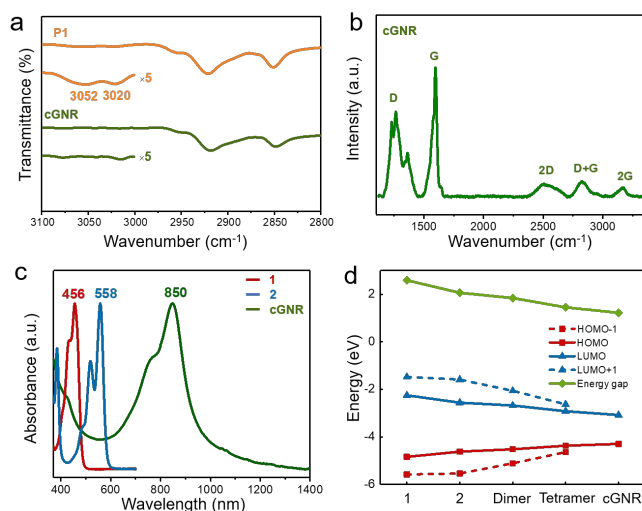


Figure 2. Spectroscopic characterizations of the cGNR. (a) FTIR spectra of **P1** and the cGNR. (b) Raman spectrum of the cGNR measured at 532 nm. (c) UV-vis absorption spectra of the cGNR in chloroform (0.1 mg mL⁻¹) and **1**, **2** in DCM (10⁻⁵ M). (d) Calculated energy level of **1**, **2**, Dimer (Figure S22), Tetramer (Figure S22), and cGNR.

Thanks to the long alkyl chain decoration at the edges and the nonplanar geometry, the cGNR can be readily dispersed in common organic solvents, including chloroform, tetrahydrofuran, and toluene, etc. Mild sonication enables the formation of green stable dispersion of the cGNR with a high concentration of 0.1 mg mL⁻¹ in chloroform. From the UV-vis-NIR absorption spectra of compounds **1** and **2** in DCM (Figure 2c), the energy gap of **2** is inferred to be 2.1 eV, which is lower than that of **1** (2.5 eV). Compared to **1** and **2**, cGNR displays a significantly red-shifted absorption to the NIR region with a maximum absorption peak at ~850 nm. The optical energy gap of cGNR is calculated to be 1.22 eV, which is quite small compared with those of the reported solution-processable GNRs^{17,21,24-26}. DFT simulation confirms the up-down confor-

mation of **cGNR** (Scheme 2b), in line with the crystal structure data of its corresponding model compounds **1** and **2**. In addition, the energy gaps of **1**, **2**, and **cGNR** are calculated to be 2.59, 2.06, and 1.22 eV, respectively, in excellent agreement with the experimental results (Figure 2d).

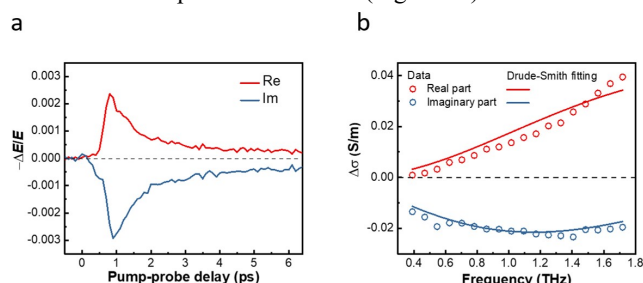


Figure 3. (a) Time-resolved terahertz photoconductivity (proportional to the relative changes in the transmitted field, $-\Delta E/E$) of **cGNR** following photoexcitation. The samples are photoexcited by a short ~ 50 fs laser pulse with the photon energy of 2.4 eV and an absorbed photon density of $1.8 \times 10^{15} \text{ cm}^{-2}$. (b) The frequency-resolved THz complex conductivity measured at 1.5 ps after photoexcitation. The solid lines represent the Drude-Smith fitting following the discussion in the main text and Supporting Information.

The excellent solution processability of the **cGNR** in various organic solvents makes it promising for optoelectronic applications. Towards this end, we further investigated the electronic transport properties of **cGNR**, both in dispersion and thin-film geometries (produced by drop cast), using ultra-fast terahertz spectroscopy. In the studies, charge carriers are optically injected into **cGNR** by a ~ 50 fs visible laser pulse, and their complex conductivity is subsequently probed by a single-cycle THz pulse (with ~ 1 ps duration). Optical-pump THz-probe spectroscopy (OTPS) measures the short-range conductivity, typically within one nanoribbon. Figure 3a illustrates the time-resolved dynamics for both the real and imaginary conductivities for **cGNR** dispersed in 1,2,4-trichlorobenzene. The sub-picosecond rise in the real conductivity indicates the optical injection of free charges into the GNRs following the photoexcitation (with the pump photon energy of 2.4 eV). The subsequent rapid decay is consistent with the formation of the bound electron-hole pairs (excitons)^{31–32}. The frequency-resolved THz photoconductive response at ~ 1.5 ps after photoexcitation is shown in Figure 3b. The data can be well accounted for by the Drude-Smith (DS) model (see SI), which describes the transport of free charges subject to backscattering due to, e.g., structural deformations^{24,33–35}. In the model, a parameter c characterizes the backscattering probability, ranging between 0 (random backscattering) to -1 (preferential backscattering). The best fit to the data yields $c = -1 \pm 0.02$. The preferential backscattering presumably occurs at the ends of the **cGNR**. Remarkably, the charge scattering time τ is found to be 57 ± 3 fs, substantially larger than those of previously studied GNRs with the armchair edge (20–30 fs)^{34,36}. Using $\mu = e\tau/m^*$, with m^* the effective mass (obtained by DFT calculations, see SI), we infer a record intrinsic carrier mobility μ of $617 \pm 32 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Finally, we compare the transport properties of GNRs in dispersion to that in the thin film (by drop cast). As shown in Figure S25, we obtain the same charge scattering τ of 58 ± 3 fs, and a c parameter of ~ -0.96 . Therefore, our THz study not only reveals a high intrinsic mobility of charge carriers in **cGNR**, but also demonstrates that the deposition of the **cGNR** into a solid film, does not introduce additional charge scatter-

ing events. On the other hand, the inferred c parameters indicate a full confinement of the charge carriers for the ribbon dispersed in solution (with $1+c=0$), and some degree of charge delocalization between ribbons on the substrates thanks to the interribbon coupling (with $1+c>0$, see SI for details).

In summary, we demonstrated the bottom-up solution synthesis of a novel **cGNR** with combined edge structures of cove, zigzag, and armchair. Model compounds **1** and **2** were also synthesized to manifest the double [4]helicene structures, resulting in a curved geometry of the corresponding **cGNR**. The **cGNR** exhibited excellent liquid-phase dispersibility and unprecedented absorption in the NIR region with a maximum peak at ~ 850 nm and a particular narrow optical energy gap of ~ 1.22 eV. THz studies revealed equally high charge scattering time (~ 60 fs) and a record high intrinsic charge carrier mobility of $\sim 600 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for GNRs. The GNRs with multi-edge structure hold great promise in many applications, including photothermal conversion, photovoltaics, and nanoelectronic devices, etc.

ASSOCIATED CONTENT

Supporting Information

Experimental details, supporting figures/tables, and calculations of the model compounds and **cGNR**.

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Funding Sources

Y. M. is grateful for the financial support from the National Natural Science Foundation of China (21774076 and 52073173) and Program of Shanghai Academic Research Leader (19XD1421700). J. D. thanks the Deutsche Forschungsgemeinschaft (DFG) for funding (SFB 858). X. F. thanks the European Union's Horizon 2020 (No 881603 Graphene Flagship Core3, No 813036 Marie Skłodowska-Curie), ERC Grant on T2DCP, German DFG (Cluster of Excellence "Center for Advancing Electronics Dresden (cfaed)" and EnhanceNano (No. 391979941) as well as the European Social Fund and the Federal State of Saxony (ESFProject "GRAPHED", TU Dresden). J. L. is grateful for the startup funding from The University of Hong Kong and the funding support from ITC to the SKL. C.C. thanks the European Commission in the framework of the ERC Grant NOC2D.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We are grateful for the assistance of Mr. Enrique Caldera Cruz from Leibniz Institute for Polymer Research Dresden for the GPC measurements. We thank F. Drescher and Prof. E. Brunner for HR-MS measurements. Diffraction data were collected on BL14.3 at the BESSY II electron-storage ring operated by Helmholtz-Zentrum Berlin; we would particularly like to acknowledge the help and support of Manfred Weiss and his group members during the experiments at BESSY II. We also appreciate the Instrumental Analysis Center at Shanghai Jiao Tong University for some analyses. S. Osella thanks the Interdisciplinary Center for

Mathematical and Computational Modelling (ICM, University of Warsaw) under the G53-8 and GB80-24 computational grants.

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TOC Graphic

Curved GNR

