Supporting Information

Solvent-Mediated Self-Assembly of Nanocube Superlattices

Zewei Quan,[†,#] Hongwu Xu,[#] Chenyu Wang,[†] Xiaodong Wen,[‡] Yuxuan Wang,[¶] Jinlong Zhu,[‖] Ruipeng Li,[§] Chris J. Sheehan,[€] Zhongwu Wang,[§] Detlef-M Smilgies,[§] Zhiping Luo*,[⊥,£] and Jiye Fang*,[†,¶]

[†]Department of Chemistry, and [¶]Materials Science and Engineering Program, State University of New York at Binghamton, Binghamton, New York 13902, USA

[#]Earth and Environmental Sciences Division, [‡]Theoretical Division, [‖]Los Alamos Neutron Science Center, and [€]Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

[§]Cornell High Energy Synchrotron Source, Wilson Laboratory, Cornell University, Ithaca, New York 14853, USA

[⊥]Department of Chemistry and Physics, Fayetteville State University, Fayetteville, North Carolina 28301, USA

[£] Microscopy and Imaging Center, Texas A&M University, College Station, Texas 77843, USA

***Corresponding authors**:

jfang@binghamton.edu

zluo@uncfsu.edu

Experimental Details:

Chemicals: Tungsten hexacarbonyl (99.9%), oleic acid (90%), and oleylamine (70%) are purchased from Sigma-Aldrich. Platinum (II) acetylacetonate (49.3-49.8% Pt), anhydrous ethanol (200 proof), and anhydrous hexane (98.5%) were received from Alfa Aesar, AAPER, and BDH, respectively. All chemicals were used as received.

Synthesis of Pt Nanocubes (NCbs): Pt NCbs were prepared using a synthetic procedure previously developed.[S1] In a typical experiment, 20 mg of platinum(II) acetylacetonate, 8.0 mL of oleylamine and 2.0 mL of oleic acid were pre-mixed at room temperature and in a three-neck round-bottom flask equipped with a Schelenk line and argon gas protection. The mixture was then heated to 130 °C with gentle stirring to form a transparent solution and maintained at this temperature for 10 min. After that, 50 mg of tungsten hexacarbonyl was added into the solution, and the temperature was subsequently elevated to 200 °C and kept for 30 min. The resultant product was isolated by centrifugation and washed with the combined use of ethanol and hexane for two cycles. The isolated Pt NCbs were dispersed in hexane or toluene with adequate concentration (0.1 M) for self-assembly use.

Self-Assembly of Pt NCbs: The substrates used for this self-assembly process include two parts: the bottom portion is a (111) surface-polished square Si wafer with dimensions of 15 mm x 15 mm, and the top layer consists of a 200 mesh Cu grid coated with a formvar film and a "light" layer of carbon. In a typical preparation, 20 µL of the stock dispersion was drop-cast onto the designed substrate, immediately covered with a weight dish (41 mm in length and 8 mm in height), and seamed with a sealing tape. It took about 1 hour for hexane and 2 hours for toluene to completely evaporate, respectively, and solid Pt NCb superlattices were received onto the Cu grid. Large-area and multiple-layered Pt NCb supercrystals were assembled in a closed vial from concentrated Pt NCb suspensions in hexane using a slow-evaporation approach developed previously.[S2]

TEM Characterizations: TEM images were recorded on a Hitachi 7000 (75kv) and FEI Tecnai G^2 F20 FEG-TEM (200 kv) electron microscopes.[S3,S4] For the 3D tomographic study, TEM images were taken at different angles with an increment of 1°, and then reconstructed by the back projection method using the FEI Xplore3D program. All images, diffraction, and tomography using the FEI Tecnai were acquired using zero energy loss electrons by excluding the inelastic

electrons with the post column Gatan Image Filter (GIF), and recorded using Gatan Tridiem 2K × 2K slow scan CCD camera.

SEM Characterizations: SEM images were obtained on a Magellan XHR 400L FE-SEM located in the Center for Integrated Nanotechnologies (CINT), Los Alamos National Laboratory.

SAXS Characterizations: SAXS determination was conducted at B_1 station of Cornell High Energy Synchrotron Source (CHESS), Cornell University. The incident beam with a monochromatic wavelength of 0.485946 Å was collimated to 100 μm in diameter for the collection of SAXS patterns. Using a *Fit2D* program available at CHESS, 2D SAXS images were integrated into "1D" patterns which are plots of the intensity as a function of 2ϑ (degree) for further analyses. We masked off two of the orientation-induced strongest spots with apparent saturation for purposes of the reasonable integration and subsequent Le Bail structural refinement.

References:

(S1) Zhang, J.; Fang, J. *J. Am. Chem. Soc.* **2009**, *131*, 18543-18547.

(S2) Quan, Z.; Loc, W. S.; Lin, C.; Luo, Z.; Yang, K.; Wang, Y.; Wang, H.; Wang, Z.; Fang, J. *Nano Lett.* **2012**, *12*, 4409-4413.

(S3) Zhang, J.; Luo, Z.; Quan, Z.; Wang, Y.; Kumbhar, A.; Smilgies, D.-M.; Fang, J. *Nano Lett.* **2011**, *11*, 2912-2918.

(S4) Zhang, J.; Luo, Z.; Martens, B.; Quan, Z.; Kumbhar, A.; Porter, N.; Wang, Y.; Smilgies, D.-M.; Fang, J. *J. Am. Chem. Soc.* **2012**, *134*, 14043-14049.

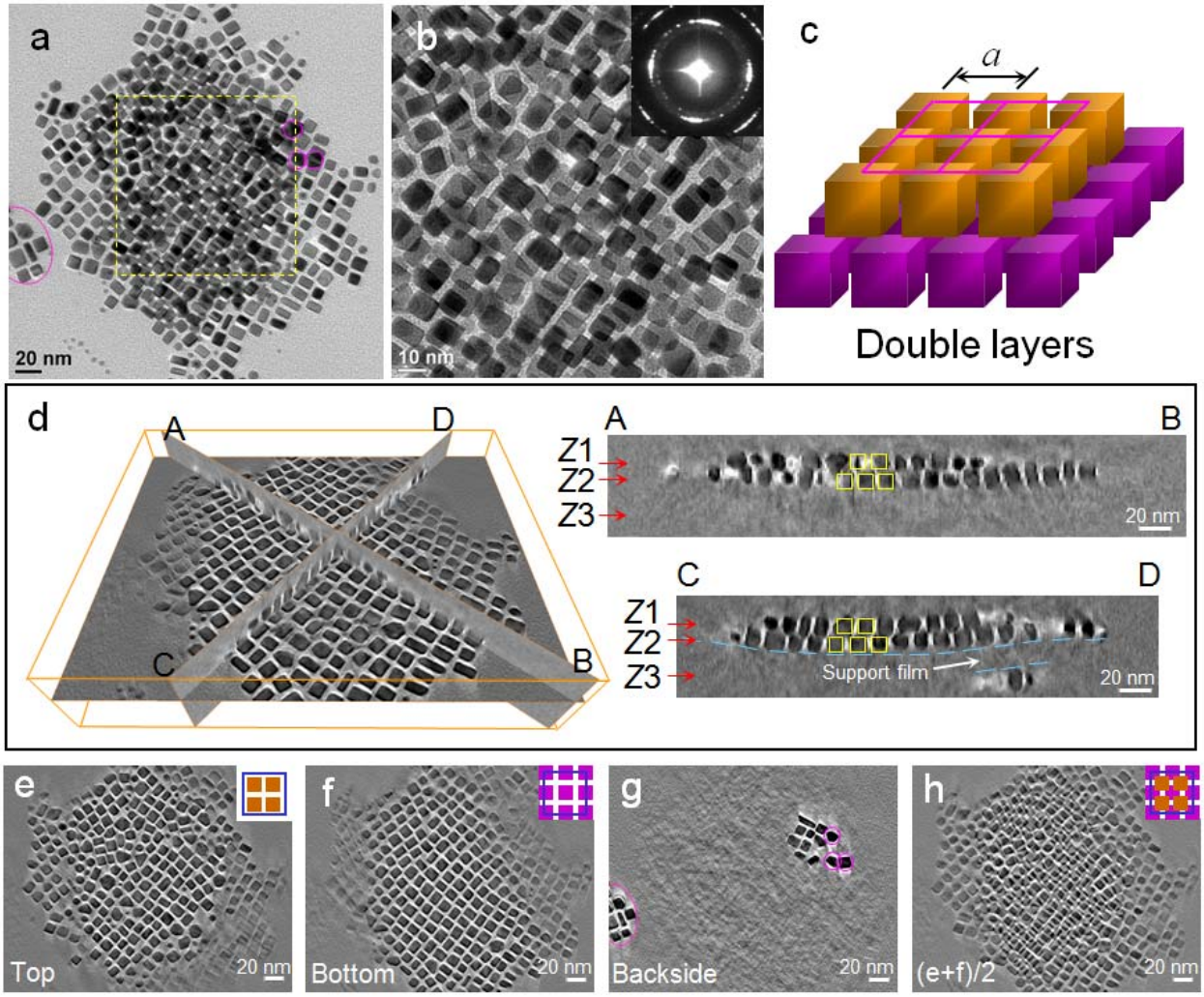

Figure S1. TEM and tomographic images of double-layer Pt NCb self-assembly generated from hexane. (a) TEM image; (b) magnified image from the framed area in (a), with an SAED pattern inserted; (c) structure model of the double-layer assembly; (d) 3D reconstruction, with two orthogonal views AB and CD showing on the right panel. Slice views at the height of z1, z2 and z3 as indicated in (d) are presented in (e)-(g) of the top layer, bottom layer, and the backside of the support film, respectively. (h) was obtained by superimposing (e) and (f) followed with a division by 2. Circled particles in (g) correspond to those in (a).

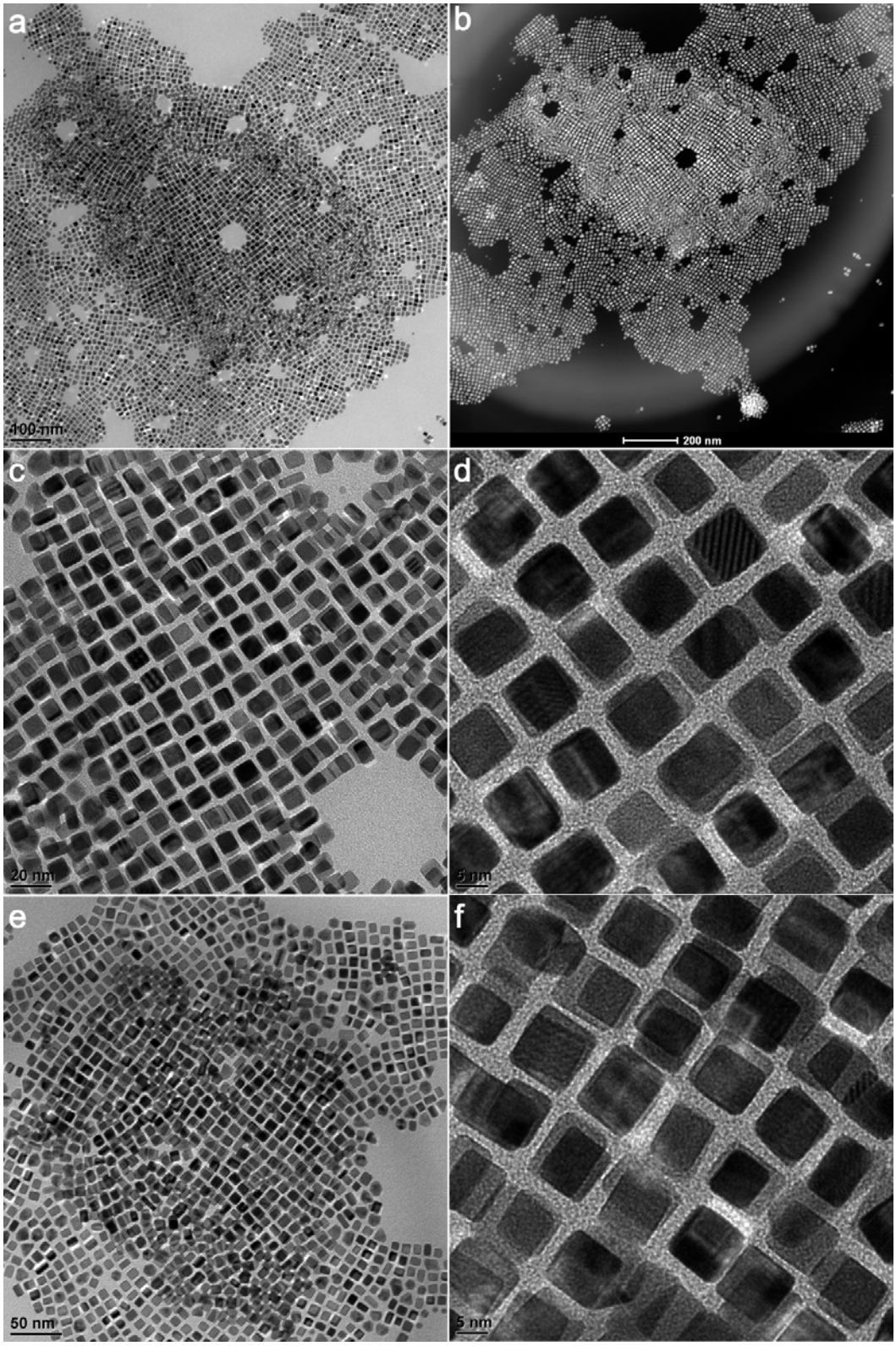

Figure S2. TEM images of Pt NCbs self-assembled from toluene as solvent at different magnifications, including two areas: I (a, c, d) and II (e-f). Note: the low-magnification image of area I is shown in (a), whereas that of area II is outside (a) and not shown. (b) is the STEM image of area I shown in (a).

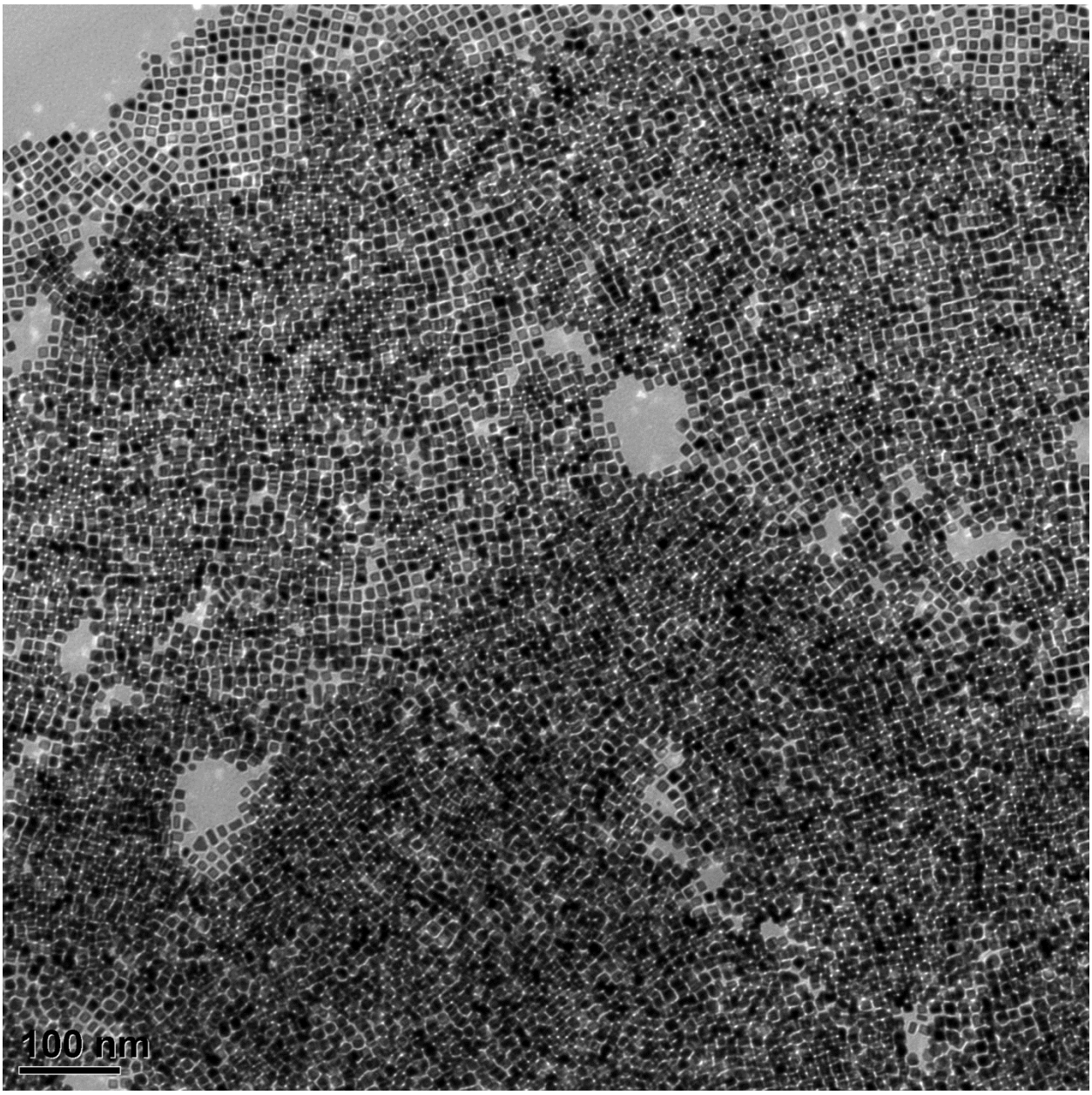

Figure S3. TEM images of Pt NCbs self-assembled from hexane as solvent at a low magnification.

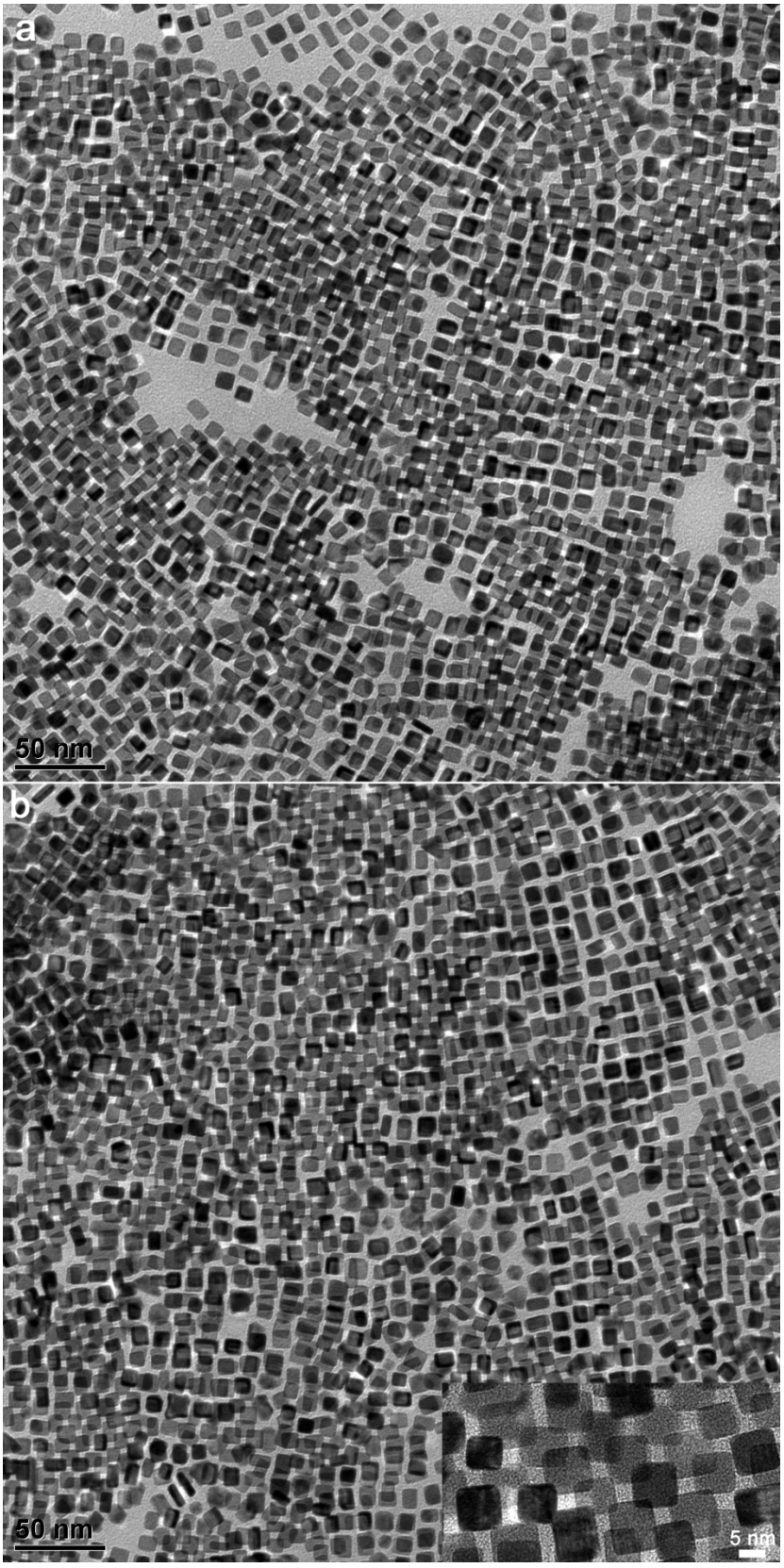

Figure S4. TEM images of mostly double-layered Pt NCbs self-assembled from hexane as solvent.

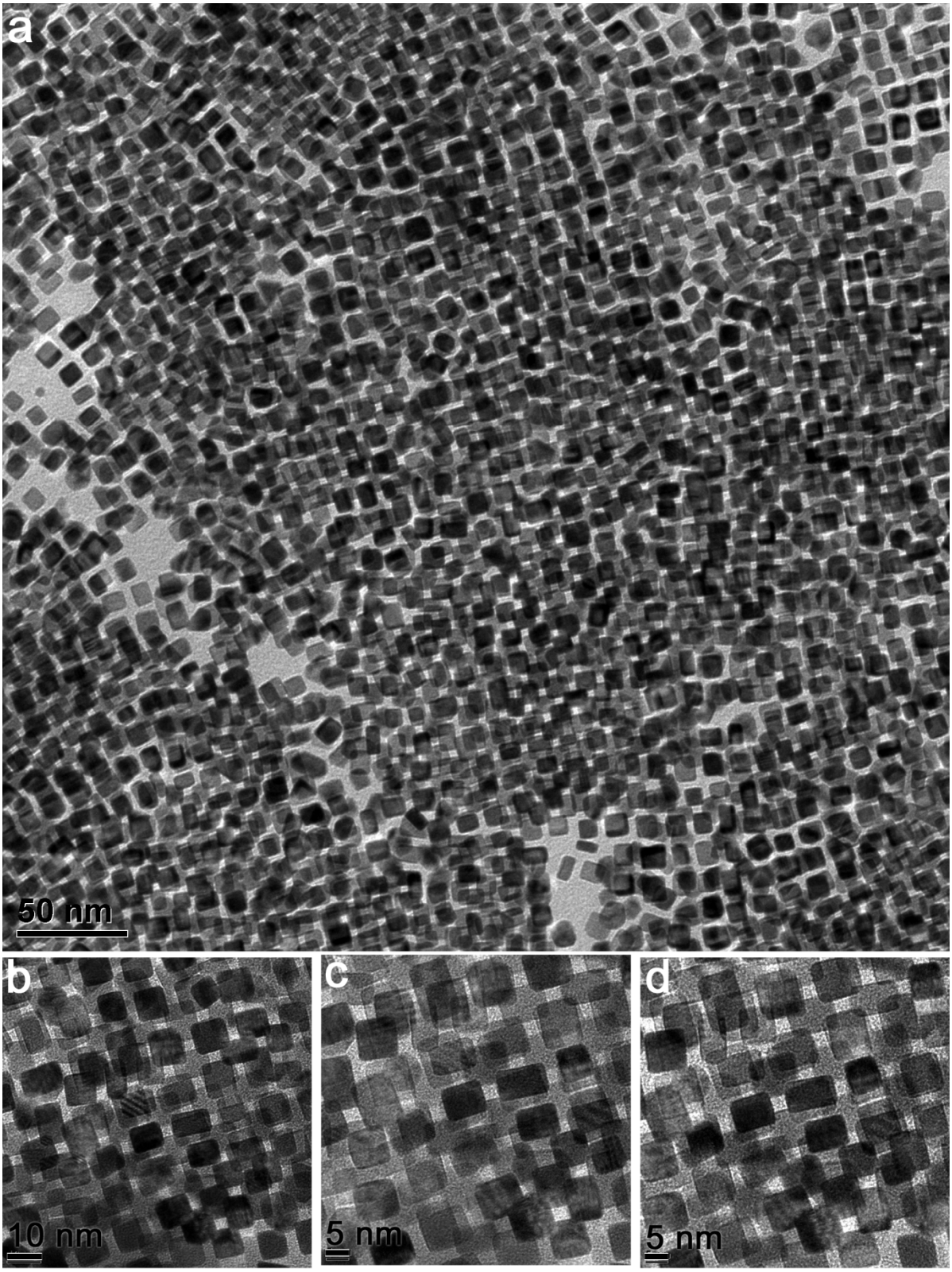

Figure S5. TEM images of mostly three-layered Pt NCbs self-assembled from hexane as solvent at different magnifications, showing a dominant *bct* superstructure.

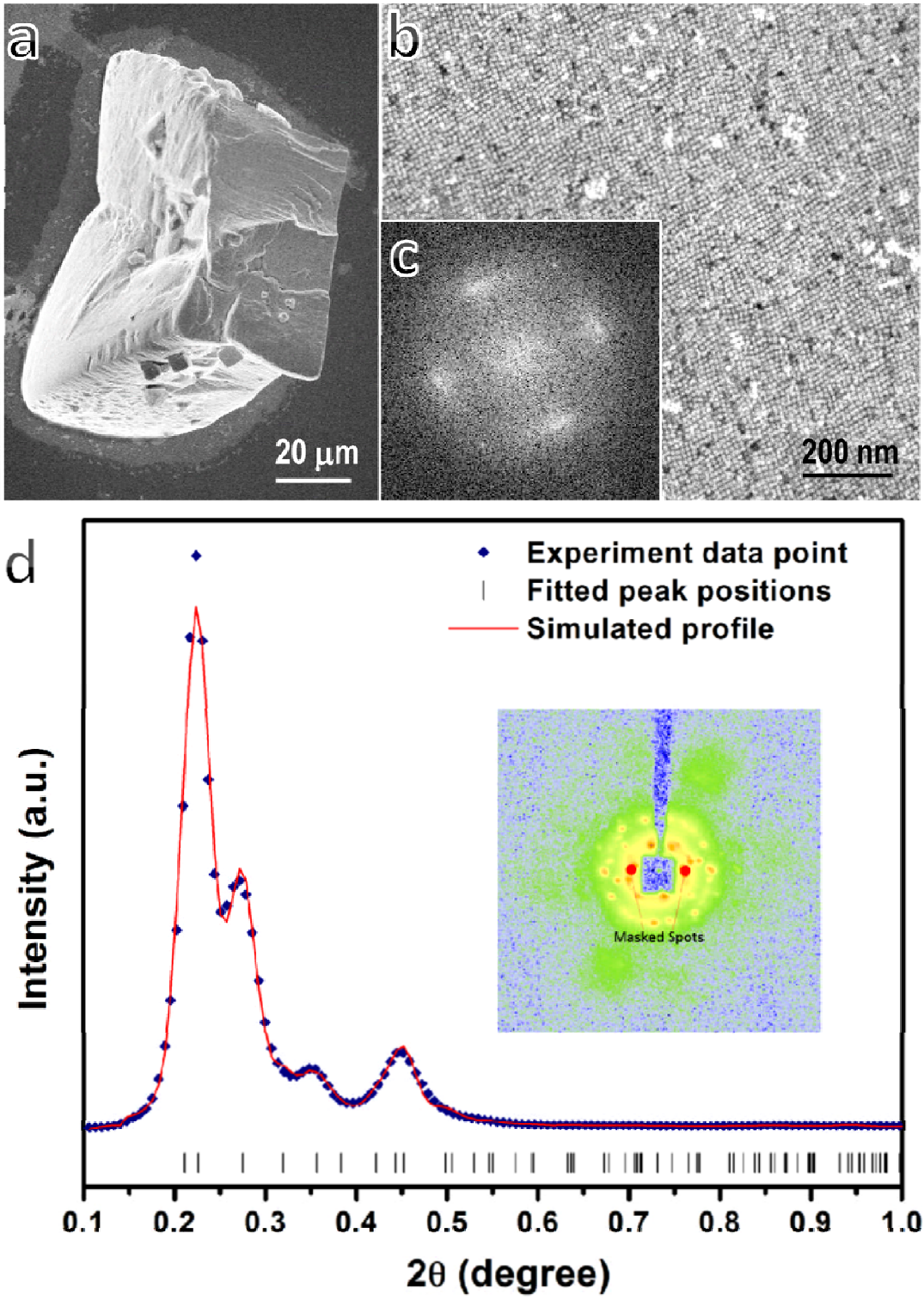

Figure S6. Characterizations on large-area and multiple-layered Pt NCb supercrystals that were slow-assembled from hexane in a capped vial. (a) and (b), SEM images with different magnifications; (c), FFT of (b); (d), a representative SAXS plot of intensity *vs* peak position (2θ) with Le Bail fitting profile, indicating a *bct* superstructure. The inset of (d) is the original 2D SAXS image pattern.

Table S1. Details of SAXS peak data on a large-area and multiple-layered Pt NCb supercrystal that was slow-assembled from hexane in a vial (ɵ, diffraction angle; d, superlattice spacing).

Peak #	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
2*ɵ* (°)	0.211	0.226	0.275	0.320	0.356	0.383	0.422	0.443	0.452	0.499	0.505	0.529
hkl	101	110	002	200	112	211	202	103	220	301	310	222
d (nm)	13.21	12.33	10.12	8.72	7.82	7.28	6.61	6.29	6.16	5.59	5.51	5.26