Micropatterning

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Imprinting Chemical and Responsive Micropatterns into Metal–Organic Frameworks**

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Metal–organic frameworks (MOFs) are at the forefront of advanced materials research and have been studied widely in the context of their potential applications in gas storage, molecular separations, sensors, and selective catalysis.[1–9] However, since MOF crystals are usually hard and brittle, their processing—including molding and patterning—is problematic, which limits the ability to combine these unique materials with sensing, photovoltaic, or electronic elements. Here, we describe a straightforward method based on wet stamping,[10,11] which allows MOF crystals to be imprinted with micropatterns of various organic chemicals. The primary underlying motivation for this research is to imprint MOFs with chemicals that change their color/appearance upon contact with specific external stimuli—in this way, micropatterned MOF crystals could sense environmental status (for example, the presence of specific sorbents) and report it in the form of visual patterns. Herein, we demonstrate in proof-of-concept experiments the ability to stamp micropatterns into single MOF crystals and their subsequent ability to perform acid/base and photochemical switching.

We have evaluated 1) MOF-5, synthesized from $Zn(NO_3)_2{\cdot}6H_2O$ and benzene-1,4-dicarboxylic acid,[1] and 2) CD-MOF-2, prepared from γ-cyclodextrin (CD) and rubidium hydroxide.[12] Both of these MOFs contain nanometer-sized cavities and 1D channels (cross-section ca. 8×8 Å^2 for both MOF-5 and CD-MOF-2) running along the *a*, *b*, and *c* crystallographic axes (Figure 1a and b). To be suitable for micropatterning over appreciable areas, the MOF crystals were grown to macroscopic dimensions of several millimeters, as illustrated in the optical images in Figure 1c and d. In the case of MOF-5, this was achieved by growing the crystals in freshly distilled diethylformamide (DEF) rather than dimethylformamide (DMF). Under solvothermal conditions, DEF decomposes into the corresponding dialkylamine[13] less rapidly than DMF, thus slowing the rate at which the dicarboxylic acid struts are deprotonated and the MOF-5 crystals grow. We emphasize the need to purify/distill the solvent prior to crystal growth. Without prior distillation of the DEF, the crystals which are obtained are typically small (tens to hundreds of micrometers) and irregularly shaped. CD-MOF-2 crystals were grown as described previously in Ref. [12] by slowly diffusing methanol vapor into an aqueous solution of γ-cyclodextrin and RbOH.

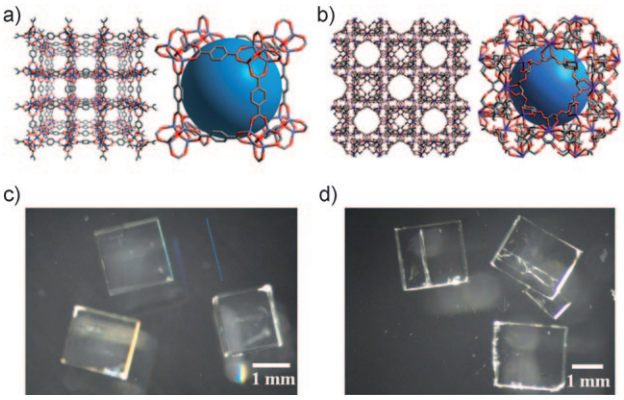

Figure 1. The channels (left) and the unit cell (right) of a) a MOF-5 crystal and b) a CD-MOF-2 crystal made from γ-cyclodextrin and RbOH. The blue spheres define the cavities in each case. c) and d) show the optical images of the millimeter-sized MOF-5 and CD-MOF-2 crystals, respectively.

The MOF crystals were patterned by a modified wet-stamping technique,[10,11] in which stamps presenting arrays of raised microscopic features were made of an agarose gel or an organogel. For CD-MOF-2, which is stable in methanol (see Section 1 in the Supporting Information), we used agarose stamps soaked in methanol. For MOF-5, which exhibits short working times in protic[14] and/or volatile solvents (see Section 2 in the Supporting Information), the stamps were made of furfurylamido-bisphenol A diglycidyl ether (FA-BADE) organogel[15] soaked in DMF. The solvents used in the stamping process did not affect the integrity of the MOF-5 and CD-MOF-2 crystals, as verified by single-crystal

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X-ray diffraction data (see Section 3 in the Supporting Information).

In a typical experiment (see Experimental Section), stamps were first soaked for several hours in a solution of a desired dye, and then the MOF crystals were placed onto the gel for several minutes (Figure 2a). This arrangement is mechanically more stable than placing the large stamp block on top of the crystal. The micropatterns printed into the crystals were then imaged by optical and/or fluorescence confocal microscopy.

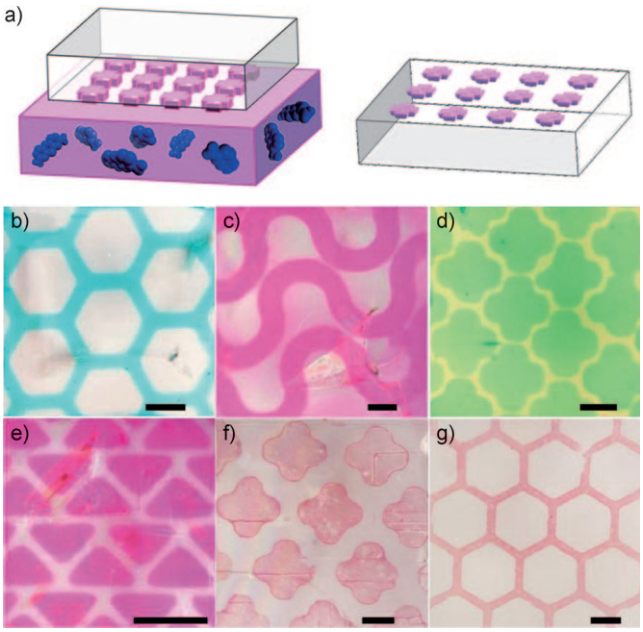

Figure 2. Printing micropatterns into MOF crystals. a) Schematic representation of the experimental arrangement whereby dye "inks" are delivered into either MOF-5 or CD-MOF-2 crystals (white blocks) from micropatterned stamps (colored violet) made of FA-BADE or agarose stamps, respectively,. b)–e) Patterns imprinted into MOF-5 using b) methylene blue (MB); c) pyronin B (PB); d) brilliant green (BG); e) pyronin Y (PY). f,g) Patterns of thionin (TH) and toluidine blue O (TBO) , respectively, printed into CD-MOF-2. Scale bars in (b) and (g) are 200 μm. Scale bars in (c)–(f) are 100 μm.

The molecules printed into the MOF-5 and CD-MOF-2 crystals included methylene blue (MB), brilliant green (BG), pyronin B (PB), pyronin Y (PY), thionin (TH), toluidine blue O (TBO), azure A (AA), azure B (AB), azure C (AC), rhodamine B (RB), methyl yellow (MY), methyl orange (MO), methyl red (MR), and 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)-3,3′,4,4′,5,5′-hexafluoro-1-cyclopentene (diaryl ethene).

While all the tested dyes diffused into MOF-5, only MY, MO, AA, AB, AC, TBO, and TH—which are known to form inclusion complexes with γ-cyclodextrins[16–20]—migrated into CD-MOF-2. We surmise this selectivity could be a result of the inherent sorting capability of γ-cyclodextrins. Interestingly, although MB, PY, and PB were also reported to form 1:1 or 1:2 inclusion complexes with γ-cyclodextrins in aqueous solutions,[21,22] we did not observe their transfer into CD-MOF-2 from MeOH-soaked stamps. In general, dyes diffused much more slowly into CD-MOF-2 than into MOF-5 (likely because of the above mentioned dye–γ-cyclodextrin interactions). The times required to print clearly visible patterns were 3–30 min for CD-MOF-2 compared with 10 s–2 min for MOF-5. As the contact times between the crystal and the gel increased, the patterns—especially in MOF-5—became blurry because of the lateral diffusion ("sideways") from the features of the stamp.[23] Interestingly, this phenomenon allowed for the creation of multicolor patters, with mixtures of dye "inks" delivered from the stamp separating on the MOF support. One example of such a patterning is illustrated in Figure 3, where a mixture of TH and PB (each

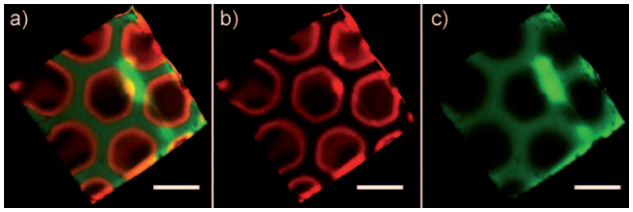

Figure 3. Multicolor micropatterns printed into MOF crystals. Fluorescent confocal images of a two-color micropattern printed using a stamp presenting an array of honeycomb features and delivering a 1:1 (each 5 mM) mixture of PB and TH dyes. PB appears red and TH appears green. Stamping time 2 min. a) A composite image; b) red/PB channel; c) green/TH channel. The slower-moving TH remains localized under the printed honeycomb features while the faster-moving PB migrates outside of the features. The exclusion of PB from below the printed regions is evident from image (b) and can be explained by a reaction-diffusion model described in detail in Ref. [10a]. All scale bars correspond to 300 μm.

5 mM) was delivered into MOF-5 from a honeycomb pattern. Since TH migrates more slowly into MOF-5 than PB (likely, because of hydrogen bonding between the primary amino groups of TH and the MOF scaffold), the TH "ink" remains localized under the stamped honeycomb features while PB migrates into the regions of the crystal between the features, thereby effectively giving a two-color micropattern akin to the reaction-diffusion patterns created previously in gel films.[10a] Features as small as about 10 μm could be resolved in all of the experiments.

Of particular interest are micropatterns based on molecules responsive to external stimuli,[24] whereby the appearance of the pattern can be used to report environmental changes. Here, we considered two such systems. In the first system evaluated, a micropattern of MO (a pH indicator) showed a colorimetric change when exposed to acidic or basic vapors (Figure 4a). The MO dye printed into CD-MOF-2 changes from yellow to red when the crystal is exposed for several seconds to gaseous hydrochloric acid, which protonates the dye. The pattern reverts to the yellow color when the crystal is exposed to ammonia gas. We verified that the acid/base cycle can be repeated (>10 times) without any noticeable decrease in the quality of the pattern or color intensity. In the second example (Figure 4b), a pattern of the photoactive diaryl ethene is invisible when the crystal is exposed to visible light, but becomes blue when the crystal is irradiated with UV light (254 nm, intensity: 10 mW cm^{-2}) for

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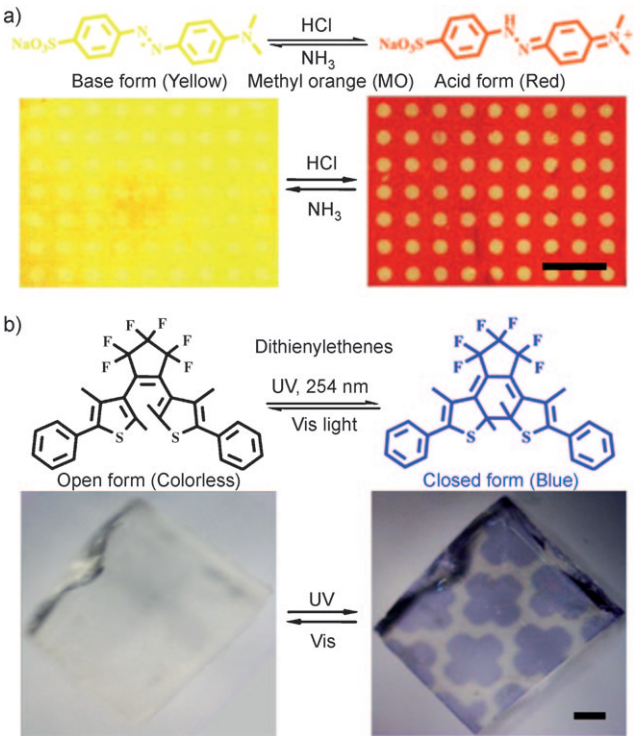

Figure 4. Reversible and responsive micropatterns printed into MOFs. a) A micropattern of methyl orange (MO) printed into CD-MOF-2 changes from yellow to red when exposed to gaseous hydrochloric acid and back from red to yellow when exposed to ammonia gas. b) A pattern printed into a MOF-5 crystal using a photoswitchable diaryl ethene which is invisible under irradiation with visible light but appears blue when exposed to UV light (intensity 10 mW cm^{-2}, wavelength 254 nm, duration of irradiation 30–60 s). All scale bars correspond to 100 μm.

30–60 s. Since the isomerization between open (colorless) and closed (blue) forms of diaryl ethenes is reversible, the switching was cycled over 300 times and the switching ability was not affected over a time scale of 24 h.

In summary, we have developed a method that allows for patterns of dyes and indicators to be imprinted into large crystals of MOF-5 and CD-MOF-2 by using either DMF-compatible organogel or MeOH-compatible agarose gel stamps, respectively. Environmental conditions—namely adjustments in the pH value or exposure to light—were monitored by visual observation of the colorimetric changes to the micropattern imprinted into the metal–organic frameworks. Beyond the proof-of-the-concept experiments we describe here, two potentially productive avenues for future research would be to develop MOF-based sensors that would report the selective sorption of small toxic gas molecules into metal–organic frameworks or to pattern MOFs with metallic patterns for use in surface-enhanced Raman spectroscopy (SERS)[25] or as light concentrators.[26]

Experimental Section

Preparation of MOF-5 single crystals: All reagents were purchased from Aldrich. Prior to use, DEF was distilled under reduced pressure. Borosilicate glass scintillation vials (20 mL) were purchased from VWR and rinsed with deionized water to remove any particulate matter, and dried at 80 °C prior to use. Freshly distilled DEF (88 mL) was added to an Erlenmeyer flask containing $Zn(NO_3)_2 \cdot 6H_2O$ (3.08 g) and benzene-1,4-dicarboxylic acid (578 mg). The mixture was stirred for 20 min or until the solids dissolved. Portions (5 mL each) were removed by syringe and injected through a 13 mm syringe filter (0.45 μm PTFE membrane) into eighteen 20 mL scintillation vials, which were then sealed with a polypropylene-lined screw cap. The vials were placed in a large crystallizing dish and heated at 85 °C for 72 h. The vials were removed and cooled to room temperature for 24 h, upon which the MOF-5 crystals were washed with fresh DMF (3 × 10 mL). Most vials produced large, millimeter-sized crystals (up to ca. 3 × 3 × 2 mm^3).

Preparation of CD-MOF-2 single crystals: γ-Cyclodextrin (1.30 g, 1 mmol) and RbOH (0.82 g, 8 mmol) were dissolved in deionized H_2O (20 mL). The solution was filtered through a 13 mm syringe filter (0.45 μm PTFE membrane) into prewashed borosilicate culture tubes (16 × 150 mm). MeOH (ca. 50 mL) was allowed to vapor diffuse into this solution over a period of two weeks. Millimeter-sized colorless cubic crystals (up to ca. 2 × 2 × 1 mm^3) were isolated and washed with MeOH (2 × 30 mL) prior to use.

Synthesis of organogel for dye mixture delivery:

a) Synthesis of gel precursors modified from Ref. [15]: Furfurylamine (FA, 96 mmol) and bisphenol A diglycidyl ether (BADE, 48 mmol) were dissolved in DMF (160 mL), followed by heating at 90 °C for two days. The reaction mixture was cooled down and stored in the dark.

b) Preparation of FA-BADE organogel: 1,1′-(Methylenedi-1,4-phenylene)bismaleimide (MBI, 6 mmol) was added to a solution of crude FA-BADE oligomer (containing about 12 mmol furfuryamido units) from step (a), before shaking the mixture for 10 mins and then leaving it to stand at room temperature for 3 days to allow complete gelation to occur.

c) Preparation of organogel stamps: A mixture of FA-BADE oligomers (30 mL) and MBI cross-linkers (9 mmol) was cast against a poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow Corning) master with micrometer features embossed on its surface. After gelation, the organogel was gently peeled off and cut into 1 × 1 × 1 cm^3 rectangular "stamps" with an array of raised micrometer features. The stamps were soaked in a DMF solution of the desired dyes (ca. 2–10 mM) for several hours.

Preparation of agarose stamps: A hot, degassed aqueous solution of high strength agarose (7 wt %, Omni Pur, EM Science, Darmstadt, Germany) was cast against a plasma-treated PDMS master with an array of micrometer-sized features embossed on its surface. After gelation at room temperature, the agarose was peeled off gently from the master and cut into ca. 1.5 × 1.5 × 1 cm^3 rectangular stamps. The stamps were then soaked in a MeOH solution of the dyes (ca. 2–10 mM) for several hours.

Printing micropatterns into MOFs: Immediately prior to use, stamps (either organogel or agarose) were placed on a glass slide with the patterned side facing up, and were blotted dry first with tissue paper and then under a stream of nitrogen. A single MOF crystal was placed onto the stamp. After the patterns were imprinted, they were analyzed either by stereomicroscopy or by fluorescence confocal microscopy on a Leica SP2 system with a Leica DMRXE7 upright microscope.

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[1] a) H. L. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276 – 279; b) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469 – 472.

[2] S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388 – 2430; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334 – 2375.

[3] O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705 – 712.

[4] D. Sun, S. Ma, Y. Ke, D. J. Collins, H.-C. Zhou, *J. Am. Chem. Soc.* **2006**, *128*, 3896 – 3897.

[5] T. K. Maji, S. Kitagawa, *Pure Appl. Chem.* **2007**, *79*, 2155 – 2177.

[6] J. L. C. Rowsell, O. M. Yaghi, *J. Am. Chem. Soc.* **2006**, *128*, 1304 – 1315.

[7] H. Frost, T. Dulren, R. Q. Snurr, *J. Phys. Chem. B* **2006**, *110*, 9565 – 9570.

[8] J. L. C. Rowsell, E. C. Spencer, J. Eckert, J. A. K. Howard, O. M. Yaghi, *Science* **2005**, *309*, 1350 – 1354.

[9] A. R. Millward, O. M. Yaghi, *J. Am. Chem. Soc.* **2005**, *127*, 17998 – 17999.

[10] a) R. Klajn, M. Fialkowski, I. T. Bensemann, A. Bitner, C. J. Campbell, K. Bishop, S. Smoukov, B. A. Grzybowski, *Nat. Mater.* **2004**, *3*, 729 – 735; b) B. A. Grzybowski, K. J. M. Bishop, C. J. Campbell, M. Fialkowski, *Soft Matter* **2005**, *1*, 114 – 128; c) B. A. Grzybowski, K. J. M. Bishop, *Small* **2009**, *5*, 22 – 27.

[11] a) B. A. Grzybowski, C. J. Campbell, *Mater. Today* **2007**, *10*, 38 – 46; b) C. J. Campbell, M. Fialkowski, R. Klajn, I. T. Bensemann, B. A. Grzybowski, *Adv. Mater.* **2004**, *16*, 1912 – 1917; c) C. J. Campbell, S. K. Smoukov, K. J. M. Bishop, B. A. Grzybowski, *Adv. Mater.* **2006**, *18*, 2004 – 2008; d) S. K. Smoukov, B. A. Grzybowski, *Chem. Mater.* **2006**, *18*, 4722 – 4723; e) C. J. Campbell, S. K. Smoukov, K. J. M. Bishop, B. A. Grzybowski, *Langmuir* **2005**, *21*, 2637 – 2640.

[12] R. A. Smaldone, R. S. Forgan, H. Furukawa, J. J. Gassensmith, A. M. Z. Slawin, O. M. Yaghi, J. F. Stoddart, *Angew. Chem.* **2010**, *122*, 8812 – 8816; *Angew. Chem. Int. Ed.* **2010**, *49*, 8630 – 8634.

[13] a) C. Paulet, T. Loiseau, G. Ferey, *J. Mater. Chem.* **2000**, *10*, 1225 – 1229; b) E. Biemmi, T. Bein, N. Stock, *Solid State Sci.* **2006**, *8*, 363 – 370.

[14] a) S. S. Kaye, A. Dailly, O. M. Yaghi, *J. Am. Chem. Soc.* **2007**, *129*, 14176 – 14177; b) K. Schröck, F. Schröder, M. Heyden, R. A. Fischer, M. Havenith, *Phys. Chem. Chem. Phys.* **2008**, *10*, 4732 – 4739; c) B. Chen, X.-J. Wang, Q.-F. Zhang, X.-Y. Xi, J.-J. Cai, H. Qi, S. Shi, J. Wang, D. Yuan, M. Fang, *J. Mater. Chem.* **2010**, *20*, 3758 – 3767.

[15] A. M. Peterson, R. E. Jensen, G. R. Palmese, *ACS Appl. Mater. Interfaces* **2009**, *1*, 992 – 995.

[16] M. Ilanchelian, R. C. Retna, R. Ramaraj, *J. Inclusion Phenom. Macrocyclic Chem.* **2000**, *36*, 9 – 20.

[17] R. J. Clarke, J. H. Coate, S. F. Lincoln, *Carbohydr. Res.* **1984**, *127*, 181 – 191.

[18] S. Hamai, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 861 – 866.

[19] M. Maafi, B. Laassis, J.-J. Aaron, M. C. Mahedero, A. M. De La Pena, F. Salinas, *J. Inclusion Phenom. Mol. Recognit. Chem.* **1995**, *22*, 235 – 247.

[20] Z.-B. Yuan, M. Zhu, S. Han, *Anal. Chim. Acta* **1999**, *389*, 291 – 298.

[21] S. Hamai, H. Satou, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2207 – 2214.

[22] R. L. Schiller, S. F. Lincoln, J. H. Coates, *J. Incl. Phenom.* **1987**, *5*, 59 – 63.

[23] When the supply of the solvent from the stamp was terminated, the printed patterns stopped "spreading" and these patterns remained stable for weeks. Also, in addition to the lateral spreading, the dyes diffused a few tens of micrometers into the MOF crystals (see Section 4 in the Supporting Information).

[24] a) A. Sidorenko, T. Krupenkin, A. Taylor, P. Fratzl, J. Aizenberg, *Science* **2007**, *315*, 487 – 490; b) R. Klajn, P. J. Wesson, K. J. M. Bishop, B. A. Grzybowski, *Angew. Chem.* **2009**, *121*, 7169 – 7173; *Angew. Chem. Int. Ed.* **2009**, *48*, 7035 – 7039; c) J. Kim, M. J. Serpe, L. A. Lyon, *Angew. Chem.* **2005**, *117*, 1357 – 1360; *Angew. Chem. Int. Ed.* **2005**, *44*, 1333 – 1336; d) P. Uhlmann, L. Ionov, N. Houbenov, M. Nitschke, K. Grundke, M. Motornov, S. Minko, M. Stamm, *Prog. Org. Coat.* **2006**, *55*, 168 – 174; e) H. S. Lim, J. T. Han, M. Jin, K. Cho, *J. Am. Chem. Soc.* **2006**, *128*, 14458 – 14459.

[25] a) K. A. Willets, R. P. Van Duyne, *Annu. Rev. Phys. Chem.* **2007**, *58*, 267 – 297; b) X. Lu, M. Rycenga, S. E. Skrabalak, B. Wiley, Y. Xia, *Annu. Rev. Phys. Chem.* **2009**, *60*, 167 – 192; c) L. E. Kreno, J. T. Hupp, R. P. Van Duyne, *Anal. Chem.* **2010**, *82*, 8042 – 8046.

[26] H. A. Atwater, A. Polman, *Nat. Mater.* **2010**, *9*, 205 – 213.

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